Changing the permeability, mineral and soil structure of clay soil with chlorine dioxide

By

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ABSTRACT

Clay particles have small particle sizes. With the addition of water, the change in volume is greater in clay soils than coarse grained soils. When clay soils are mixed with a coarse-grained soil, the shrink and swell potential of the mixed soil will decrease. Chlorine dioxide is commonly used as a disinfectant or to control algae growth in sedimentation and flocculation basins. This chemical is used to kill bacteria in soil as well. Another use of chlorine dioxide is to increase the permeability of sandstone formations through the reaction of clays in these formations. The aim of this study is to determine if the increase in permeability as observed in the field can be replicated in the laboratory, by using the same concentration of chlorine dioxide that is used in agriculture to kill bacteria in the soil.

The soil was treated with diluted chlorine dioxide to investigate the effect on the soil mineralogy and soil structure. Two different soils were used for these experiments. The first experiment was conducted with a clay soil. The second was a mixture of clay soil at the bottom with a coarse-grained soil on top to simulate different scenarios.

Chlorine dioxide was mixed with water at different concentrations and introduced into the soil at a constant rate with a drip system. The chlorine dioxide is applied once then every third day for two weeks and then four litres of clean water was introduced into the soil with the same drip system. The soil was then dried and prepared for tests.

X-Ray Fluorescence and X-Ray Diffraction was done on the soil to determine the mineralogy. A sieve analysis gave the particle size distribution for each sample. CT scan and scanning electron microscope tests were done to compare the soil structure before and after the experiment. A falling head permeability tests was also done on an untreated and treated sample to compare drainage of the soil.

This study showed the mineralogy of the soil is not affected by chlorine dioxide. The CT scan showed the voids increase after the chlorine dioxide treatment. The scanning electron microscope showed the particles coalesced into flocculated layers, but the scans does not confirm the increase in void ratio from the CT scan. Particle size distribution does not show significant changes after the chlorine dioxide treatment. Chlorine dioxide treatment improved the drainage of the clay soil. Therefore, this treatment can be used to improve the permeability of clay soil.

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List of Definitions

ARB – Antibiotic Resistant Bacteria

ARG – Antibiotic Resistant Gene

DDL – Diffuse Double Layer

HCl – Hydrochloric Acid

HF – Fluorine Acid

LL – Liquid Limit

PI - Plasticity Index

PL – Plastic Limit

ppm – parts per million

SEM – scanning electron microscope

XRD - X-Ray Diffraction

XRF - X-Ray Fluorescence

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CHAPTER 1

1. Introduction

1.1 Background

Clay soils have a low permeability, because of the small pore spaces in the soil. Mud acid (HF and HCl mixture) can be used to increase the permeability of clay soil. The HF in the Mud Acid mixture react with clay and silicates. Chlorine dioxide is used to improve the permeability of subterranean hydrocarbon bearing sandstone formations. The chlorine dioxide reacts with the clay and the silicates the same as the acid mud mixture to increase the permeability of clay (Suchfield, 1991). Chlorine dioxide is used to kill bacteria in soil in the agricultural field. In the agriculture chlorine dioxide is used at a lower concentration than to improve the permeability of sandstone formations.

A farmer used chlorine dioxide in his vineyards and the growth of the plants improved after the treatment. There was less water building up at the surface of the clay soil after the chlorine dioxide was introduced into the soil. The use of chlorine dioxide at smaller concentrations seems to improve the drainage of soil as well. Figure 1-1 shows the area where the test material was collected. The arrow on figure 1-2 shows a map of the geology at the site where the soil was collected. The geology of the soil in this area is Malmesbury Shale.

Figure 1-1 Area where the test material was sourced

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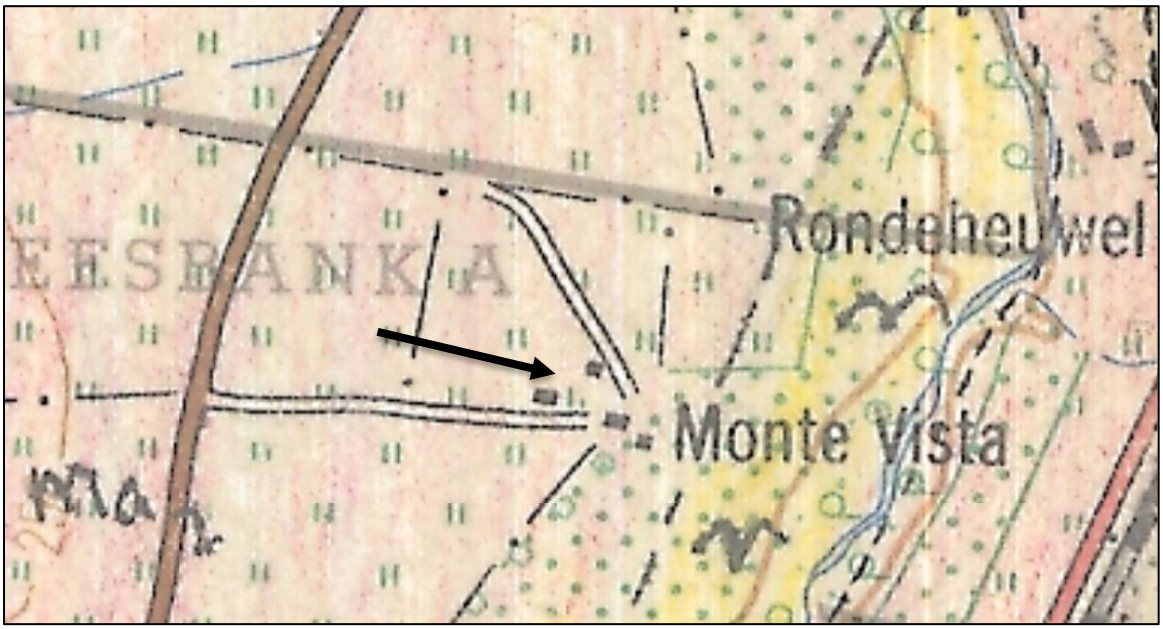

Figure 1-2 Geology of the site (Council for Geoscience)

1.2 Motivation for research

Chlorine dioxide has been tested on sandstone formation to increase the permeability of these formations. According to previous studies the ideal chlorine dioxide concentration to use in sandstone is 1000ppm - 3000ppm (Suchfield, 1991). The purpose of this study is to test if the chlorine dioxide concentration used in agriculture have the same effect as the concentration used on sandstone formations, and if so, can Chlorine dioxide then be used at lower concentrations to increase the permeability of clay soil.

1.3 Problem Statement

Clay soils have small pore spaces and the water will drain slower as it has a lower permeability, than a sandy texture soil with large pore spaces. Chlorine dioxide can react with the clay in a soil to increase the permeability at a concentration of 1000ppm-3000ppm (Suchfield, 1991). In agriculture 2000ppm chlorine dioxide is diluted to kill bacteria in the soil (G Gebers 2018, personal communication, 19 July). This study will investigate whether the concentration used for agriculture can increase the permeability of clay soil as well. Figure 1-3 shows the site where the samples had been taken to see the effect of chlorine dioxide on the permeability, mineral and soil structure of clay soil.

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Figure 1-3 Site where the soil was taken for the experiments

1.4 Objectives

The first objective of this study was to do a literature survey on the behaviour of expansive soils, clay minerals followed by the known uses of chlorine dioxide in general and in soils. The second objective was to introduce chlorine dioxide into the soil with a drip system. The last objective was to compare the permeability, mineral and soil structure of the soils with reference to the void ratio and the particle size distribution before and after the chlorine dioxide experiment.

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1.5 Thesis layout

The purpose of the study was to test the effect of chlorine dioxide on the mineralogy and the soil structure of clay. The following chapters are used to present the study:

Chapter 1 - Introduction to the research and provide background information regarding the topic.

Chapter 2 – Literature study on the soil behaviour of clay, the three common clay minerals known to be expansive. The study also includes the uses of chlorine dioxide in soil.

Chapter 3 - Describes the sample preparation of the samples and methodology used to obtain results.

Chapter 4 - Results of all the tests done on untreated samples and the chlorine dioxide treated samples.

Chapter 5 - Interpretation of tests, resulting in selective further testing.

Chapter 6 – Conclusion of the study with obtained results. Provided recommendation for further studies.

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CHAPTER 2

2. Literature study

2.1 Expansive soil

2.1.1 Introduction

If a soil has potential to swell or shrink when the moisture content varies then it is generally referred to as an expansive or heaving soil. Expansive soil causes more damage to the infrastructure than any other natural disaster. Uneven movement as well as the magnitude of the deformation in expansive soil causes damage to structures. The deformation is larger than the elastic deformation therefore the classic elastic or plastic theories are not able to predict the movement. The design and construction of projects are more in expansive soils are more complicated, because there is a lack in the understanding of the soil behaviour of these expansive soils. The risk can be reduced by recognising the expansive soil and being careful with the design and construction processes. Research is important to gather more information to improve the knowledge regards to expansive soils and designs will be safer (Nelson and Miller, 1992).

There are three important phases in the investigation process. The first phase is the reconnaissance that include observations in the field or aerial and geological maps must be used to identify the soil type in the surrounding area. Local experience must not be disregarded, and this information is critical to define the scope for further investigations. Secondly, the preliminary investigation confirms if there are expansive soils on the site. Subsurface sampling and laboratory testing can be done as part of the investigation to classify the soil profile and to determine the shrink-swell potential. A more detailed investigation is recommended based on the outcome of the preliminary investigation. The last phase is a detailed investigation that is made up of a detailed profile of the soil along with the soil properties and the shrink-swell potential. It is difficult to obtain truly undisturbed samples, but with good quality field work it is possible to get the necessary acceptable samples. The results will be more accurate if the samples are undisturbed so the detailed investigation must be planned carefully (Nelson and Miller, 1992).

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2.1.2 Swell and shrinkage

Swelling in expansive soils is influenced by several factors such as the change in soil water content that disturb the stress equilibrium. If the total stress increase in the soil because of the particle rearrangement, the interparticle forces will increase as well. Clay minerals have a negative charge along platelets and the edges are charged positive. The negative charges on the clay mineral are balanced with the water in the soil. The cations in the soil water are attached to the surface of the platelets with electrical forces. Electrochemistry of the soil water and the negatively charged surfaces form a bond that is part of the interparticle forces. There are other factors that disturb the equilibrium in terms of the interparticle force field, for example the van der Waal surface forces. During swelling the volume of the soil will increase and then the effective stress will decrease (Nelson and Miller, 1992; Knappett and Craig, 2012).

The ideal condition is that the internal electrochemical forces and the external forces are in equilibrium. When the equilibrium is disturbed by the change in soil water chemistry, the charge on the particle's surface will change. Swell and shrink behaviour in expansive soils is when the spacing between particles change and to restore equilibrium the particles adjust the spacing. The behaviour of these soils have a major impact on the engineering industry (Nelson and Miller, 1992).

In the engineering industry these soils cause damage to structures. Heaving and lifting of structures can be caused by differential movement because of the swelling pressures in the soil. The volume change is uneven through the soil and this disturbance results in failure of structures. Figure 2-1 shows foundation cracks that are caused by expansive soil (Mokhtari and Dehghani, 2012). The damage is done over time by expansive soil. Poor construction methods however can also contribute (King, no date).

Figure 2-1 - Foundation cracks (King, no date)

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Fine-grained soil that is rich in clay minerals can absorb a substantial amount of water that increase the volume. When the soil is dried out, shrinking and cracking occurs on the surface. Consequently, the surface tends to be very hard. The soil will swell on re-wetting, but the cracks will not close perfectly. Sediment fills the shrinkage cracks and when swelling occurs the soil is unable to close the cracks. This process results in increasing swelling pressure (Mokhtari and Dehghani, 2012). Figure 2-2 show an expansive soil that is dried out and the pen illustrate the width of the cracks (King, no date).

Figure 2-2 - Soil cracks (King, no date)

2.1.3 Swell potential

The soil properties influence the basic internal force field of a soil (Nelson and Miller, 1992). Minerals like smectite, nontronite, chlorite, montmorillonite and vermiculite determine the natural expansiveness of a soil if the particle sizes are extremely fine. The expansive potential will increase if the soil contains a larger amount of these minerals. Minerals like illites and kaolinites only influence the swell potential when the particles sizes are small. Non-swelling minerals like quartz and carbonate diminish the expansive effects of the swelling minerals thereby reduce the overall activity (Holtz, Kovacs and Sheahan, 2011).

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Activity in the soil usually occur near the surface zone which is approximately 3m deep but varies based on climate conditions. Underground excavations can experience swell and shrink as well even if it is under the surface zone. (Mokhtari and Dehghani, 2012). The following formula is used to calculate the activity (Ac) of the soil. Table 2-1 show the activity of the three main clay mineral groups with their typical activity (Nelson and Miller, 1992; Springman and Davison, 2000).

$$Ac = \frac{PI}{\%\, weight < 2\mu m}$$

Table 2-1 - Activity of clay minerals

Mineral	Activity (Ac)
Kaolinite	0.33 – 0.46
Illite	0.9
Montmorillonite (Ca)	1.5
Montmorillonite (Na)	7.2

The increase in concentration and valence of cations will decrease the swell potential of the clay. Therefore, when magnesium cations are in the soil water, the soil will swell less than if the soil water contains potassium. The negatively charged face of the clay particle and the cations in die solution form a diffuse double layer (DDL). This semi-permeable layer is formed by the clay particle. Interparticle repulsive forces are generated when two DDL's overlap and this overlap create swelling pressure within the soil. The thickness of the DDL is affected by the concentration and valence of the cations and the swell potential will increase as the thickness of the DDL increase. The cations are held in higher concentrations near the DDL of the particles surface. The difference in concentration at the DDL and in the free water between particles creates osmotic pressure. Additional forces may be generated by the hydration process of the salt if the soil is dry. These forces are called osmotic suction (Sridharan and Jayadeva, 1982; Nelson and Miller, 1992; Holtz, Kovacs and Sheahan, 2011).

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Clays that are dispersive trend to be less expansive than flocculated clays. Cement can be used to reduce the swell potential of a clay. The dry density gives an indication on the swell potentials. The repulsive forces will be greater if the particles are closer spaced. Therefore, a clay with a higher dry density may result in a larger swell potential. Expansive soils are more frequently classified by the clay content or plasticity of the soil (Huang *et al.*, 2019).

The initial moisture condition will have an influence on the soil as expansive soil bind better with water than other soils and has higher suction. If the initial soil profile was wet, the soil will lose water more easily when exposed to drying conditions but will shrink more if the profile was relatively dry. The upper part of a soil profile is the active zone and there will be sideways displacement, also known as heave, when there is variation in the moisture content (Elarabi, 2015).

The change in climate affects the precipitation and evapotranspiration and that influence the seasonal moisture variation. The increase in temperatures and decrease in rainfall cause a change to the moisture in the soil. Areas with short wet periods will experience more season heave in semi-arid climates. The fluctuation in the water table contribute to moisture and if the water table is shallow it is a source of moisture that will affects the heave in the active zone. Around a poorly graded foundation ponding or pipes that leak can provide the soil with water at great depths. Therefore, the movement of expansive soil must be predicted with the effect of the change in climate on these soils (Nelson and Miller, 1992; Mitchell, 2013).

Vegetation reduce the moisture content in the soil through transpiration. Therefore, the moisture content can vary where the vegetation is different. Soil with high permeability and cracks allow the water to move faster, which increases the rate of swelling within the soil. Evaporation will affect the moisture content in the soil. The increase in temperature will also let the moisture expand under the buildings or pavements to cooler areas (Elarabi, 2015).

Conditions like the in situ, stress history, loading or soil profile will have an influence on the swell potential of the soil. Normally consolidated soil is less expansive than the same over consolidated soil. Swell pressure can increase over time, but the swell under small loading can be unaffected over time. Wetting-drying cycles can be used to reduce swelling and after a while tests have shown that the swell does not reduce anymore (Nelson and Miller, 1992).

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The volume change can be determined by the magnitude of the surcharge pressure at a certain moisture content and density. Swell can be reduced with externally applied loads, because these loads balances out the interparticle repulsive forces. Soil profiles where the clay minerals stretch from the surface till below the active zone tend to have more movement than clays covered with a non-expansive layer (Nelson and Miller, 1992).

2.2 Mineralogy

2.2.1 Introduction

The state of particles in soil can be solid, liquid or gas and the hardness ranges from soft organic material to hard rock. The shape, size and properties of the soil are mainly controlled by the mineralogy of the soil. These factors affect the physical and chemical properties of a soil. Therefore, it is important to have knowledge of which minerals are present in the soil and their behaviour. The term clay can refer to a mineral class or the particle size. The engineering classification states that the clay particle size usually is smaller than 0.002mm. Isomorphous substitution in octahedral and tetrahedral positions are when space in the ideal crystal structure is occupied by other cations without changing the crystal structure. For example aluminium replaces silicon or ferrous iron replaces magnesium (Mitchell, 1993; Springman and Davison, 2000).

2.2.2 Kaolinite

Kaolinite originate from aluminium silicate minerals and feldspar that have been chemically weathered. The colour of kaolinite is white with red from iron oxide or another mineral can change the colour to be blue or green. This mineral has a triclinic crystal system and not monoclinic, because there is distortion in the oxygen-to-oxygen bonds from the octahedral and alternating silica sheets. It is rare to find a trioctahedral 1:1 mineral that is not in a mixture. Therefore, the structural formula for kaolinite is $(OH)_8Si_4Al_4O_{10}$. Interlayer bonding consist of both van der Waal forces and hydrogen bonds. These bonds are strong enough to prevent interlayer swelling if water is present. Different minerals can form in the kaolinite subgroup due to the variations in the stacking of layers. Figure 2-3 show a schematic diagram for the mineral structure of kaolinite (Mitchell, 1993; Vayne and Harrison, 2000).

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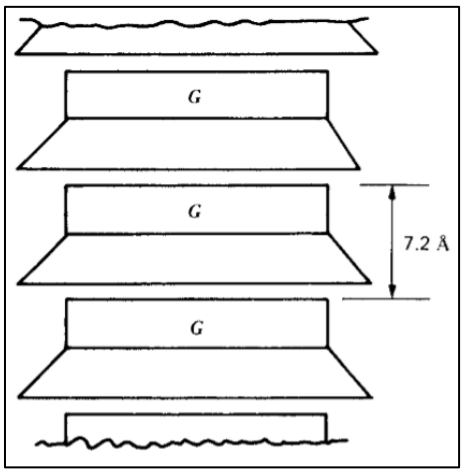

Figure 2-3 - Kaolinite structure (Mitchell, 1993)

The charge on the edges of kaolinite particles is dependent on the pH of the environment. When they are in a low pH environment, the charge will be positive and negative in a high pH environment. The mineral has low exchange capacity in acidic conditions and a high exchange capacity in alkaline conditions. The balancing cations must bond with the external edges and layers, because the interlayers of kaolinite do not separate. It has a specific area of 10-20 m^2/g of dry clay. Figure 2-4 show an electron photomicrograph of kaolinite (Mitchell, 1993).

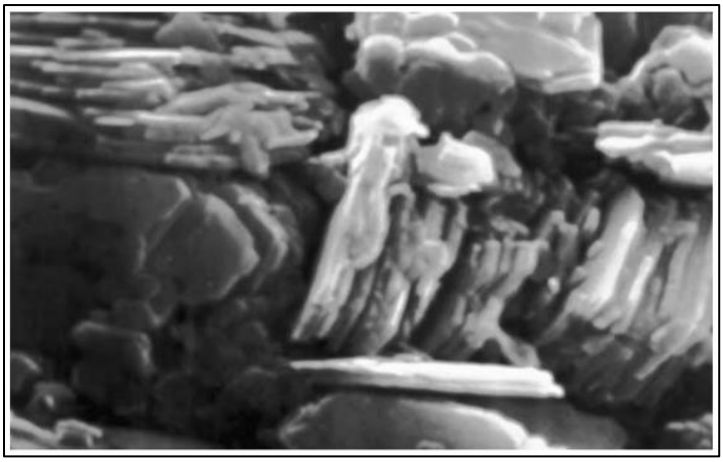

Figure 2-4 - Electron photomicrograph of kaolinite (Mitchell, 1993)

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2.2.3 Mica

The structure of illite is similar to muscovite mica and it is also known as hydrous mica. The structure of muscovite is pyrophyllite that consist of three-layer silica-gibbsite-silica sandwich. Muscovite has a structural formula of $(OH)_4K_2(Si_6Al_2)Al_4O_{20}$. This mineral has a di-octahedral mineral structure and the octahedral layer only contains Al^{3+} ions. In illite less Al^{3+} ions and more Si^{4+} ions. The muscovite mineral is held together with electrostatic forces between the aluminium silicate layers and the K^+ ions. The particles of illite have a specific area of 65-100 m^2/g which makes it smaller than that of mica and illite contains less potassium. Along with the particle size the sheet in the mineral structure can differ (Mitchell, 1993; Marini, 2007).

The octahedral sheet of illite may contain more iron, aluminium and magnesium. Iron-rich illite is also known as glauconite and occur as green pellets. Extensive isomorphous substitution take place in illite and it has a charge deficiency of 1.3 – 1.5 per cell unit. This is mostly located in the silica sheets and the non-exchangeable potassium layers balance it out. Figure 2-5 show a typical structure of muscovite and illite and figure 2-6 show an electron photomicrograph of illite. The particles of illite are small, flaky and mixed with other non-clay and clay materials (Mitchell, 1993).

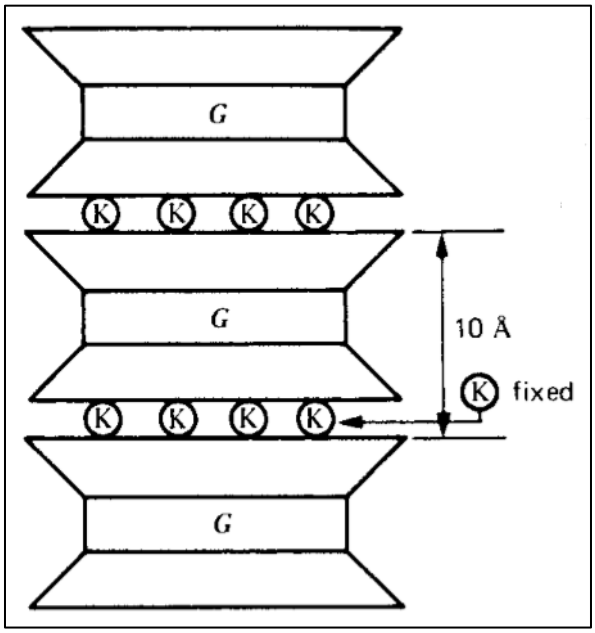

Figure 2-5 - Illite and muscovite structure (Mitchell, 1993)

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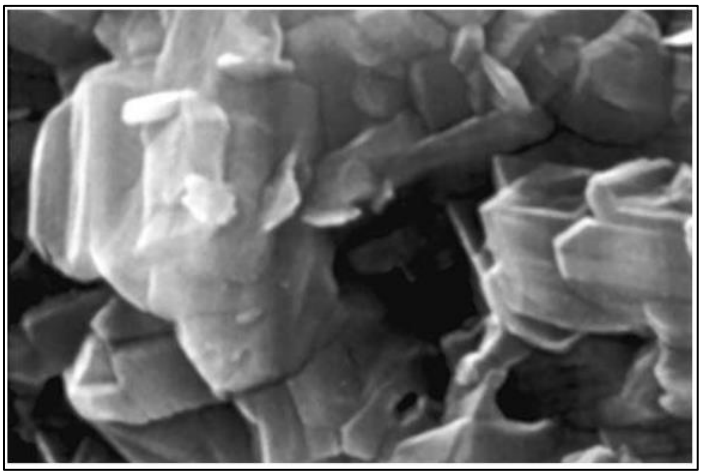

Figure 2-6 - Electron photomicrograph of illite (Mitchell, 1993)

2.2.4 Smectite

Smectite minerals are the most important source of swelling in expansive soils. This mineral gives the soil the adhesive property that is important to prevent soil erosion. Smectite minerals absorb water easily that can cause destruction in the form of landslides. They have a theoretical formula of $(OH)_4Si_8Al_4O_{20} \cdot nH_2O$ where n is the interlayer, if there is no isomorphous substitution. The interlayer bonds are van der Waal forces that form a weak bonding between layers. Adsorption of polar liquids or water will separate the layers that allow swelling. The hydration energy and interlayer cations in smectite hydrate is greater than the attractive forces therefore swelling will take place (Dixon, Weed and Dinauer, 1989; Mitchell, 1993).

Extensive isomorphous substitution occur in the smectite mineral group with silicon and aluminium. Aluminium can be substituted in one-for-one or three-for-two. The new structure can dioctahedral that is the montmorillonite subgroup or trioctahedral that is the saponite subgroup. The charge deficiency after the substitution is around 0.66 per cell but can vary between 0.5 and 1.2 per cell. Magnesium will replace aluminium with this charge deficiency counts. The minerals in the smectite group have a lot of unbalanced substitutions therefore the cation exchange capacity is 80 to 150 meq/100g (Mitchell, 1993).

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The specific area of montmorillonite can be very large if compare with illite or kaolinite, because the mineral occurs as thin equidimensional flakes. The primary area that does not take the interlayer zone surface area into account ranges between 50 to 120 m^2/g. With the interlayer zone surface area included the total area can be as high as 840 m^2/g. Figure 2-7 show the electron photomicrograph of montmorillonite (Mitchell, 1993).

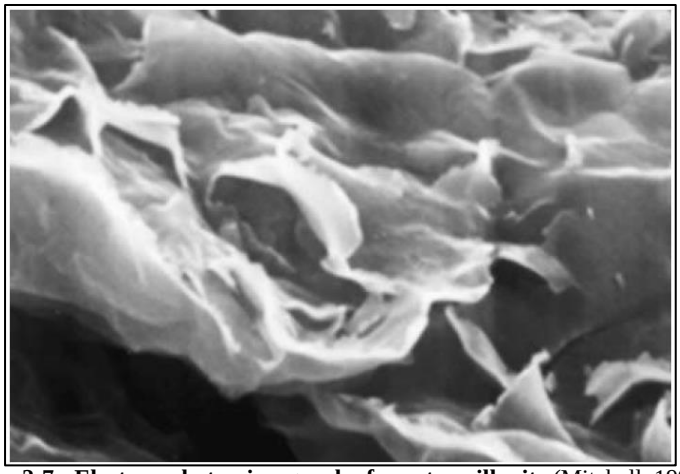

Figure 2-7 - Electron photomicrograph of montmorillonite (Mitchell, 1993)

2.3 Chlorine Dioxide

2.3.1 Basic physical and chemical properties

Chlorine dioxide (ClO_2) is a biocide that is environmentally safe, and its properties make it more powerful than most (Mason John, Kielman Gary, 1999) . The structure of the molecule contains two chlorine atoms, but the physical and chemical properties of chlorine dioxide make it different from that of chlorine. The chemical properties of chlorine dioxide are closer to the properties of oxygen than chlorine. The properties described below are what makes this chemical so popular to use in different industries (Mason John, Kielman Gary, 1999).

Chlorine dioxide is an oxidising biocide like ozone, but not a metabolic toxin. It disrupts the transport of nutrients through the cell wall of the organism by not disrupting the metabolic process. Metabolic toxins kill organisms when they absorb the biocide, but many organisms are mostly inactive or in a dormant state that is why metabolic toxins kill these organisms ineffectively. These biocides must be used at larger concentrations and more frequently to be as effective as oxidising biocides. The micro-organisms build

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up resistance to a metabolic biocide like ammonia compounds. Therefore, in practice they must be alternated to prevent resistance development against the substance by organisms. Oxidising biocides do not need to be alternated, because organisms cannot develop resistance against it (Mason John, Kielman Gary, 1999).

Chlorine dioxide is less reactive than ozone and chlorine and most organic compounds will be consumed by ozone and chlorine. Chlorine dioxide only reacts with a few compounds like secondary and tertiary amines, reduced sulphur compounds and some reactive and highly reduced organics. Chlorine dioxide will have a more stable residue than ozone and chlorine due to its selectivity. Chlorine dioxide dissolve better in hydrocarbons and emulsions than water. Therefore, chlorine dioxide will penetrate the protective bacterial slime and other artificial hydrocarbon layers against other biocides (Mason John, Kielman Gary, 1999).

Chlorine dioxide and ozone are the only biocides that are soluble as a true gas. Ozone is more unstable therefore chlorine dioxide is more effective to use. Chlorine dioxide will transport too areas like headspaces and pipe walls, because the molecule remains a true gas. This chemical is used to control bacteria in medical waste, because the physical properties allow it to penetrate most substances. Chlorine dioxide has a free radical that is why the chemical will react immediately if possible with little or no effect (Mason John, Kielman Gary, 1999).

2.3.2 Factors that make Chlorine dioxide environmentally friendly

- Chlorine dioxide is an oxidising biocide and it does not build up toxic biological material.
- Toxin carcinogenic by products does not form under water treatment conditions, because no chlorination by-products form.
- It is not a strong oxidant and that is why toxic organic or inorganic by-products cannot form.
- Chlorine dioxide along with its by-products chlorite and chlorate break down to sodium chloride that is harmless in the environment (Mason John, Kielman Gary, 1999).

Appendix A shows government restrictions against chlorine dioxide.

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2.3.3 Oxidation Potential

The metabolism of micro-organisms and their ability to survive are affected by the oxidation reduction potential of the substance they live in. Chlorine dioxide has an oxidation state of +IV and is a compound of chlorine. The molecule is highly energetic and volatile while diluted in an aqueous solution. Chlorine dioxide can react violently with reduced agents and does not chlorinate. Chlorine dioxide oxidases effective due to the selective oxidant that reduces it to chlorite (ClO_2^-) with its one-electron transfer. Approximately 50-70% of chlorine dioxide is converted to chlorite (ClO_2^-) and 30% converted to chlorate (ClO_3^-) and chloride (Cl^-) in drinking water. The oxidation reaction of chlorine dioxide look as follow:('Alternative Disinfectants and Oxidants Guidance Manual', 1999)

$$ClO_{2(aq)} + e^- = ClO_2^- \qquad (1) \qquad E^o = 0.954V$$

Here are three other half reactions that take place:

$$ClO_2^- + 2H_2O + 4e^- = Cl^- + 4OH^- \qquad (2) \qquad E^o = 0.76V$$

$$ClO_3^- + H_2O + 2e^- = ClO_2^- + 2OH^- \qquad (3) \qquad E^o = 0.33V$$

$$ClO_3^- + 2H^+ + e^- = ClO_2 + H_2O \qquad (4) \qquad E^o = 1.152V$$

2.3.4 Generation process

Chlorine dioxide is very soluble especially in chilled water. The chemical stays in solution as a dissolved gas although it does not hydrolyse at all. The solution is extremely volatile, and the chlorine dioxide can be removed from the aqueous solution with recarbonation with carbon dioxide or aeration. Above 12°C the radicals are in gaseous form and react 7-10 million times slower than the hydrolysis rate of chlorine gas with water ('Alternative Disinfectants and Oxidants Guidance Manual', 1999).

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Chlorine dioxide is never shipped or store commercially as a gas, because it is explosive when the concentration exceeds 10% by the volume of air. The ignition temperature is above 130°C. Gaseous chlorine dioxide can be released above the solution in a high concentration aqueous solution. Sodium chlorite is used as a precursor feedstock chemical to produce chlorine dioxide in most chlorine dioxide commercial generators. Newer generators produce a diluted gaseous chlorine dioxide at a continuous rate rather than a aqueous solution ('Alternative Disinfectants and Oxidants Guidance Manual', 1999).

2.3.4.1 Methods of generations

The following reactions show how sodium chlorite can be used to generate chlorine dioxide by reacting with gaseous chlorine ($Cl_{2(g)}$), hydrochloric acid (HCl) and hypochlorous acid ($HOCl$). Figure 2-8 shows commercial generators for chlorine dioxide ('Alternative Disinfectants and Oxidants Guidance Manual', 1999).

$$2NaClO_2 + Cl_{2(g)} = 2ClO_{2(g)} + 2NaCl \quad (5)$$

$$2NaClO_2 + HOCl = 2ClO_{2(g)} + 2NaCl + NaOH \quad (6)$$

$$5NaClO_2 + 4HCl = 4ClO_{2(g)} + 5NaCl + 2H_2O \quad (7)$$

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GENERATOR TYPE	MAIN REACTIONS Reactants, byproducts, key reactions, and chemistry notes	SPECIAL ATTRIBUTES
ACID-CHLORITE: (Direct Acid System)	$4HCl + 5NaClO_2 \rightarrow 4ClO_{2(aq)} + ClO_3^-$ • Low pH • ClO_3^- possible • Slow reaction rates	Chemical feed pump interlocks required. Production limit ~ 25-30 lb/day. Maximum yield at ~80% efficiency.
AQUEOUS CHLORINE-CHLORITE: (Cl_2 gas ejectors with chemical pumps for liquids or booster pump for ejector water).	$Cl_2 + H_2O \rightarrow [HOCl / HCl]$ $[HOCl/HCl] + NaClO_2 \rightarrow$ $ClO_{2(g)} + H/OCl^- + NaOH + ClO_3^-$ • Low pH • ClO_3^- possible • Relatively slow reaction rates	Excess Cl_2 or acid to neutralize NaOH. Production rates limited to ~ 1000 lb/day. High conversion but yield only 80-92% More corrosive effluent due to low pH (~2.8-3.5). Three chemical systems pump HCl, hypochlorite, chlorite, and dilution water to reaction chamber.
RECYCLED AQUEOUS CHLORINE OR "FRENCH LOOP"™ (Saturated Cl_2 solution via a recycling loop prior to mixing with chlorite solution.)	$2HOCl + 2NaClO_2 \rightarrow 2ClO_2 + Cl_2 + 2NaOH$ • Excess Cl_2 or HCl needed due to NaOH formed.	Concentration of ~3 g/L required for maximum efficiency. Production rate limited to ~ 1000 lb/day. Yield of 92-98% with ~10% excess Cl_2 reported. Highly corrosive to pumps; draw-down calibration needed. Maturation tank required after mixing.
GASEOUS CHLORINE-CHLORITE (Gaseous Cl_2 and 25% solution of sodium chlorite; pulled by ejector into the reaction column.)	$Cl_{2(g)} + NaClO_{2(aq)} \rightarrow ClO_{2(aq)}$ • Neutral pH • Rapid reaction • Potential scaling in reactor under vacuum due to hardness of feedstock.	Production rates 5-120,000 lb/day. Ejector-based, with no pumps. Motive water is dilution water. Near neutral pH effluent. No excess Cl_2. Turndown rated at 5-10X with yield of 95-99%. Less than 2% excess Cl_2. Highly calibrated flow meters with min. line pressure ~ 40 psig needed.
GASEOUS CHLORINE-SOLIDS CHLORITE MATRIX (Humidified Cl_2 gas is pulled or pumped through a stable matrix containing solid sodium chlorite.)	$Cl_{2(g)} + NaClO_{2(s)} \rightarrow ClO_{2(g)} + NaCl$ • Rapid reaction rate • New technology	Cl_2 gas diluted with N_2 or filtered air to produce ~8% gaseous ClO_2 stream. Infinite turndown is possible with >99% yield. Maximum rate to ~1200 lb/day per column; ganged to >10,000 lb/day.
ELECTROCHEMICAL (Continuous generation of ClO_2 from 25% chlorite solution recycled through electrolyte cell)	$NaClO_{2(aq)} \rightarrow ClO_{2(aq)} + e^-$ • New technology	Counter-current chilled water stream accepts gaseous ClO_2 from production cell after it diffuses across the gas permeable membrane. Small one-pass system requires precise flow for power requirements (Coulombs law).
ACID/PEROXIDE/CHLORIDE	$2NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2ClO_2 + O_2 + NaSO_4 + H_20$	Uses concentrated H_2O_2 and H_2SO_4. Downscaled version; Foam binding; Low pH.

Source: Adapted from Gates, 1998.

Figure 2-8 - Commercial generators ('Alternative Disinfectants and Oxidants Guidance Manual', 1999)

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Chlorine dioxide is generated in two steps with a chlorine-chlorite solution. Hypochlorous acid and hydrochloric acid form from the reaction of chlorine gas and water. The acid reacts with sodium chlorite to form chlorine dioxide. It is important that the ratios of the acid and the sodium chlorite is controlled, because insufficient chlorine will lead to unreacted chlorite. If there is excess chlorine the chlorate ions will form which is an oxidation product of chlorine dioxide. Direct acidification of sodium chlorite can be used to generate chlorine dioxide. Hydrochloric acid is preferred for this type of generator and it is reported that multiple stoichiometric reactions occur in this process ('Alternative Disinfectants and Oxidants Guidance Manual', 1999).

These generation systems are referred to as the conventional system. Excess chlorine can be used to lower the pH of the reaction and the sodium chlorite solution can be fully utilized. Figure 2-9 shows a design of a conventional chlorine dioxide generator ('Alternative Disinfectants and Oxidants Guidance Manual', 1999).

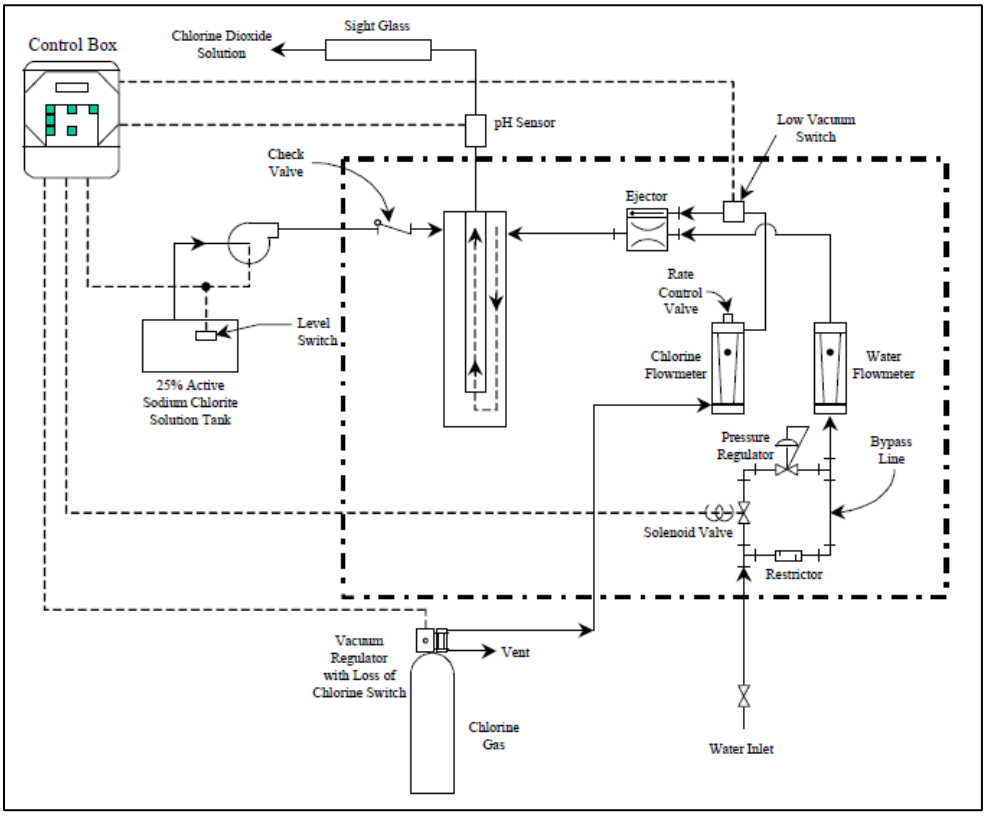

Figure 2-9 - conventional chlorine dioxide generator. ('Alternative Disinfectants and Oxidants Guidance Manual', 1999)

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2.3.4.2 PH Effect on generators

Sodium hydroxide is a by-product of the reaction between sodium chlorite and hypochlorous acid. This by-product is also a stabilizer for sodium chlorite that can cause the pH of the solution to increase. High pH levels slow the generation process of chlorine dioxide and makes the reactions less efficient. The aqueous chlorine solution will oxidize directly to chlorine dioxide if the pH is very low. Reaction (5) will proceed after the oxidation the gaseous chlorine ('Alternative Disinfectants and Oxidants Guidance Manual', 1999).

2.3.5 Uses of chlorine dioxide

Chlorine dioxide is used to clean drinking water at approximately 500 facilities in the United States. This chemical is primarily used to control taste and odour in water and to oxidise manganese and iron. Chlorine dioxide can also react to manganese and iron in their soluble form. The purpose of the application will depend on the type of treatment plant and the quality of the raw water. This chemical is now used as a substitute for chlorine in the peroxidation process in water treatment plants. Chlorine dioxide can control the algae growth in sedimentation and flocculation basins as well.('Alternative Disinfectants and Oxidants Guidance Manual', 1999; Long, Hulsey and Hoehn, 2010).

The blue/green algae known as cyanobacteria water blooms, produce toxic substances like microcystins. This substance can cause diseases like liver damage and activity that lead to tumour growth. Cyanobacteria cells is not removed by the conventional water treatment process of flocculation, sedimentation and filtration. Therefore, other chemicals like ozone, permanganate, chlorine or UV photolysis is used to remove these bacteria. Chlorine dioxide can be used to remove these bacteria cells as well due to the strong oxidation potential of this chemical. Chlorine dioxide remove these bacteria more efficient than permanganate, because chlorine dioxide decomposes contaminants in the water without generating disinfection by-products. Whereas permanganate generate manganese dioxide that effect the water quality. Chlorine dioxide is used in agriculture as a disinfectant as well in soils. (Wu *et al.*, 2012)

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Antibiotic resistant bacteria (ARB) are more commonly found in soils where livestock congregate or where antibiotics is used. The application of manure onto soil increase the antibiotic resistant genes (ARG) of the bacteria and the diversity of these genes. These ARB and ARG can be transferred from the agricultural setting to human. Antibiotic resistant tuberculosis cases were reported in 2009 and 2011 in Iran. Chlorine dioxide is used to inactivate microorganisms and to remove organic compounds in animal husbandries instead of chlorine. Chlorine dioxide can be used to inactivate the ARBs in the soil and it can be used to disinfect the soil. Figure 2-10 shows a graph that compare the kill value of 7 of the strongest antibiotic resistant isolates at different chlorine dioxide dosages. (Wu and Xu, 2019)

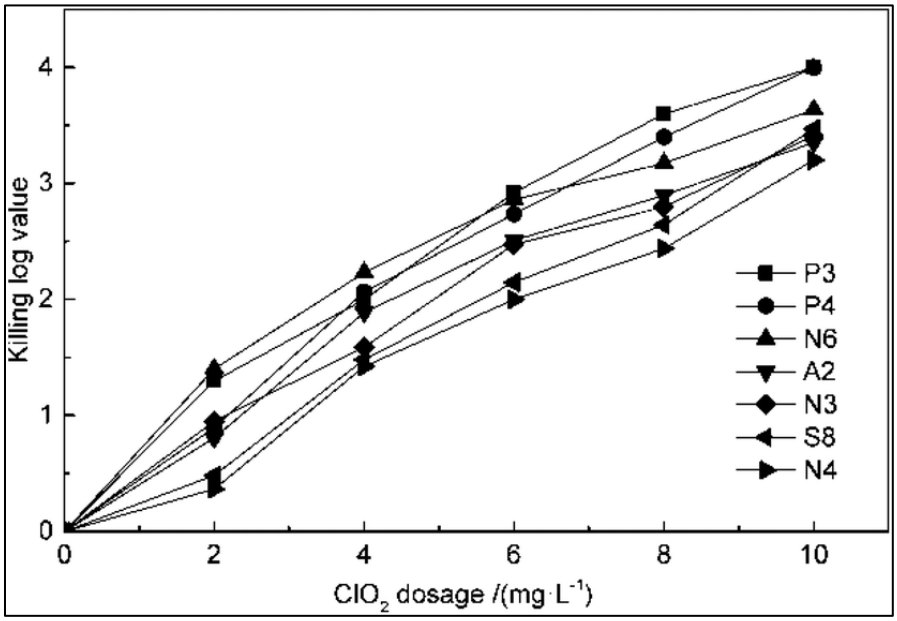

Figure 2-10 Killing value of antibiotic resistant isolates with the use of chlorine dioxide.(Wu and Xu, 2019)

The low permeability of clay soil can be treated with mud acid which is a mixture of HF and HCl. In this process the HF react with the clay and silicates to increase the permeability. Chlorine dioxide is used to improve the permeability of subterranean hydrocarbon bearing sandstone formations. The clay in this formation restrict the flow of liquids and this cause the formations to have a low plasticity. The chlorine dioxide reacts with the clay and the silicates the same as the acid mud mixture to increase the permeability of clay. According to (Suchfield, 1991) the most preferable concentration of chlorine dioxide in the aqueous solution must be between 1000 and 3000 ppm. Hydro-fracturing on the other hand does not increase the native permeability of the sandstone formations but the fracturing process cause the rocks itself to fracture that create alternative flow geometry. (Suchfield, 1991)

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Chapter 3

3. Methodology

3.1 Chlorine dioxide bulk experiment

In the agriculture chlorine dioxide is used at 50litres/ha. There are approximately 3300 vineyard trees planted on one hectare. Each tree receives approximately 15ml of chlorine dioxide and are watered with about 4litres every third day. Therefore, the concentration chlorine dioxide each tree receives is approximately 3.75ml/l. Two additional concentrations was used to compare the results of the different concentrations. Samples 1, 2 and 3 had a concentration of chlorine dioxide to water of 3.75ml/l, 7.5ml/l and 11.25ml/l respectively. The experiments were done indoors where the samples are not exposed to direct sunlight, because chlorine dioxide loses its effectiveness when exposed to UV light.

An ionic surfactant experiment was also performed to compare the results with the chlorine dioxide treated sample to identify if chlorine dioxide shows the same changes as the ionic surfactant. The methodology of the ionic surfactant experiment was the same chlorine dioxide experiment and the used concentrations the same. The samples were labelled with T1IS# where the # indicates the sample number.

The first set of experiments is done in two parts. The first part is clay soil covered with a coarse grained soil and the samples are marked as T1CS#. The second part is with a clay soil only and the samples are marked with T1C#. The second set of experiments was done with clay soil only to ensure consistent results. The second set is labelled as T2C# where the # indicates the sample number. The methodology for the experiments was the same, only the concentration of the mixtures changed.

Approximately 23kg of clay soil was placed in a container as shown in figure 3-1. Mix the chlorine dioxide, with a concentration of 2000ppm, with four litres of water. The aqueous chlorine dioxide solution was introduced into the soil with a drip system. After the aqueous chlorine dioxide solution is introduced into the soil, introduce four litres of water every third day into the soil through the drip system for two weeks. After the two weeks the bulk chlorine dioxide experiment is complete and the soil can be removed to prepare for laboratory testing.

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Figure 3-1 Container used for the bulk chlorine dioxide experiment

The experiment where the clay soil is covered with a coarse grained soil, the 23kg clay soil is covered with 10kg coarse grained soil. The rest of the experiment is the same as described above. After the two weeks the coarse grained soil is removed from the clay and the clay soil is then ready for laboratory testing.

3.2 Permeability test with chlorine dioxide experiment

The chlorine dioxide experiment will be different for the permeability test and the bulk experiment. The sample must be compacted then treated with chlorine dioxide to not disturb the soil structure of the sample before the permeability test is performed. Two falling head permeability tests will be performed on the untreated sample and on chlorine dioxide treated samples. The falling head permeability test done as describe by Manual of Soil Laboratory Testing volume 2 (Head, no date). The method is adjusted to introduce chlorine dioxide into the sample before the permeability test is performed.

Use a mould with diameter and height of 75mm and 130mm for the compaction. Compact the sample at three layers of 55 blows with a 50mm compact hammer. Place a geotextile mat on the surface at the bottom of the sample with a 1mm sieve on top. Fill the rest of the mould on the bottom with 13mm stones. Attach the bottom of the mould to a base plate and ensure the connection between the mould and the base plate is sealed with a rubber. To saturate the sample, submerge the mould and baseplate in water

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for 6 days. Remove the sample from the water after the saturation process is completed. Connect an extension to the mould with a height of 85mm and sealed the connection with a rubber. Place a geotextile mat on the surface at the top of the sample with a 1mm sieve on top. Fill the extension with 13mm stone.

Mix 30ml of chlorine dioxide, with a concentration of 2000ppm, with four litres of water. The compacted sample has a mass of approximately 3.5kg. Scale the 4030ml aqueous chlorine dioxide solution for a 23kg sample down to 613ml for a 3.5kg sample. Pour the 613ml aqueous chlorine dioxide solution into the extension at let the solution flow through the sample.

After the aqueous solution flowed through the sample attach a plate to the top of the extension and ensure the connection is sealed with a rubber. Bolt the cover plate to the base plate to ensure all the connection are sealed. Submerge the apparatus in water and connect the two inlets on the cover plate to the manometer system shown in figure 3-2. One inlet will be sealed off in the manometer and the other inlet is attach so that water will flow through the sample. Measure the time taken for the water level to drop from reference point three to two and from two to one. Document the measurements and use the following formula to calculate the permeability.

$$k_T = 3.84 \times \frac{aL}{At} \log_{10}\left(\frac{h1}{h2}\right) \times 10^{-5} \quad m/s$$

Where:

k_T	Permeability
a	Area of the manometer
L	Height of the sample
A	Area of the sample
t	Time
h	Reference height

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Figure 3-2 Manometer system for the permeability test

The final result of the permeability must be given at a temperature of 20 ºC, therefore the correction factor is estimated from the graph in figure 3-3. The correction factor is multiplied with the test result to calculate the final permeability of the samples.

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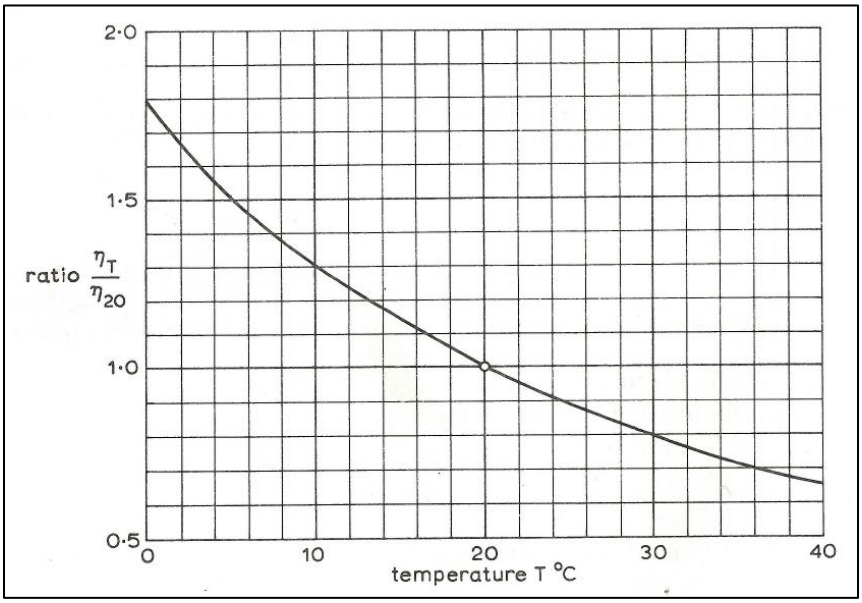

Figure 3-3 Temperature adjustment graph for permeability (Head, no date)

3.3 Sieve analysis

Grading must be done on the soil to determine the different particle sizes. Sieve analysis is used to obtain the grading done in the laboratory. The size of the sample must be a comparative representation of the experiment. The sample is predominantly clay, therefore a wet sieve analysis must be done. The fraction that passing the sieves from the hydrometer sieve analysis will be used to complete the particle size distribution curve.

Method A1 in the TMH-1 manual is used to do the sieve analysis. The sample is poured through a 19mm riffler with an even stream. This process is repeated until 2 kg sample is obtained and then soaked in water for 24 hours. The sample is then washed through a 0.425 mm sieve. The remainder of the sample is placed in a moisture oven again. Thereafter the sample is placed into a set of sieves that are placed on a vibration machine to determine the grading. The soil on each sieve is weighed and documented. Appendix D shows the set of sieves used in this method. (*Standard Methods of Testing Road Construction Materials*. Second, 1986)

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3.4 Hydrometer

Hydrometer test is used to measure the ratio between a liquid and water that is called the specific gravity. The cylindrical stem of a hydrometer contains a scale that is used to measure the specific gravity. The bulb at the bottom is filled with lead or mercury to ensure it float upright (Lemon, 2013).

The hydrometer test is done by using method A6 in TMH-1 manual. A 2 kg sample is dried in a moisture oven at 110 °C. The sample is sieved through the same set of sieves as used in section 3.2. Place 100 g of the sample left on the 0.425 mm sieve in a glass beaker and add 400 ml distilled water. To ensure the particles do not stick together add 5ml of each sodium oxalate and sodium silicate. Thereafter mix the sample thoroughly and rested for 24 hours.(*Standard Methods of Testing Road Construction Materials*. Second, 1986)

The sample is mixed for 15 minutes and poured it in a Bouyoucos cylinder. The cylinder is filled until the meniscus reaches the 1205ml mark with the hydrometer in the mixture. The cylinder is shaken and placed in a 20°C thermostat water cylinder. After one hour the hydrometer is inserted gently and document the reading. The Bouyoucos cylinder is removed from the thermostat water cylinder and shake it well. The hydrometer is insert again and document the reading after 40 seconds. After the hydrometer test is completed a sieve analysis must be conducted on the sample. (*Standard Methods of Testing Road Construction Materials*. Second, 1986)

The sample is washed through a 0.075 mm sieve and place the remainder of the sample into the 110 °C oven over night. Again the sample is placed into a set of sieves that are placed on a vibration machine to determine the grading. The soil on each sieve is weighed and documented. Appendix D indicates the fraction passing each sieve. (*Standard Methods of Testing Road Construction Materials*. Second, 1986)

The following formulas will be used to calculate the percentage coarse sand, fine sand, silt and clay in the soil mortar.

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$$P_1 = \frac{(S_m - S_f)}{S_m} \times 100$$

Where:

P1 percentage coarse sand

Sm percentage soil mortar in total sample.

Sf percentage fine soil in total sample.

$$P_2 = \frac{S_f(100 - F)}{S_m}$$

Where:

P2 percentage fine soil

F 40 second hydrometer reading

$$P_3 = \frac{S_f(F - C)}{S_m}$$

Where:

P3 percentage silt

C one hour hydrometer reading

$$P_4 = \frac{S_f \times C}{S_m}$$

Where:

P4 percentage clay

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$$P_5 = F \times \frac{S_f}{100}$$

Where:

P5 percentage silt and clay

3.5 Atterberg limits

The Atterberg tests are used to define the boundaries between the states of consistency. Figure 3-4 show the different states and the three limits on the boundaries. The difference between the liquid limit (LL) and the plastic limit (PL) is referred to as the plasticity index (PI). Colloid size particles are generally smaller than 0.001mm. Clay particles are predominantly colloidal size and therefore surface forces control their behavior(Nelson and Miller, 1992). The British soil classification system divide fine soils into ten classes based on their plasticity and LL values. Figure 3-5 show the plasticity chart for the British soil classification system where the plasticity range include low, intermediate, high, very high and extremely high. The A-line on the graph is a boundary between the clay soils and silt or organic soil. (Springman and Davison, 2000; Knappett and Craig, 2012).

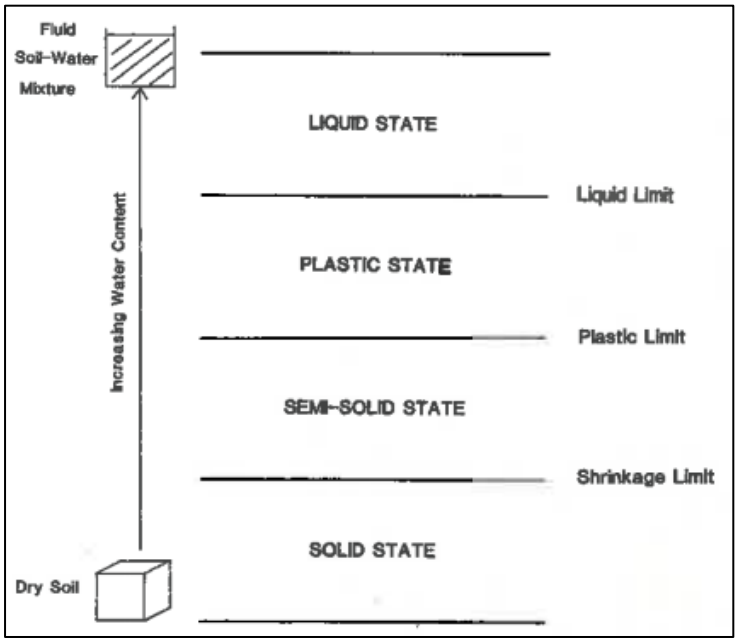

Figure 3-4 - Different states of a soil (Nelson and Miller, 1992)

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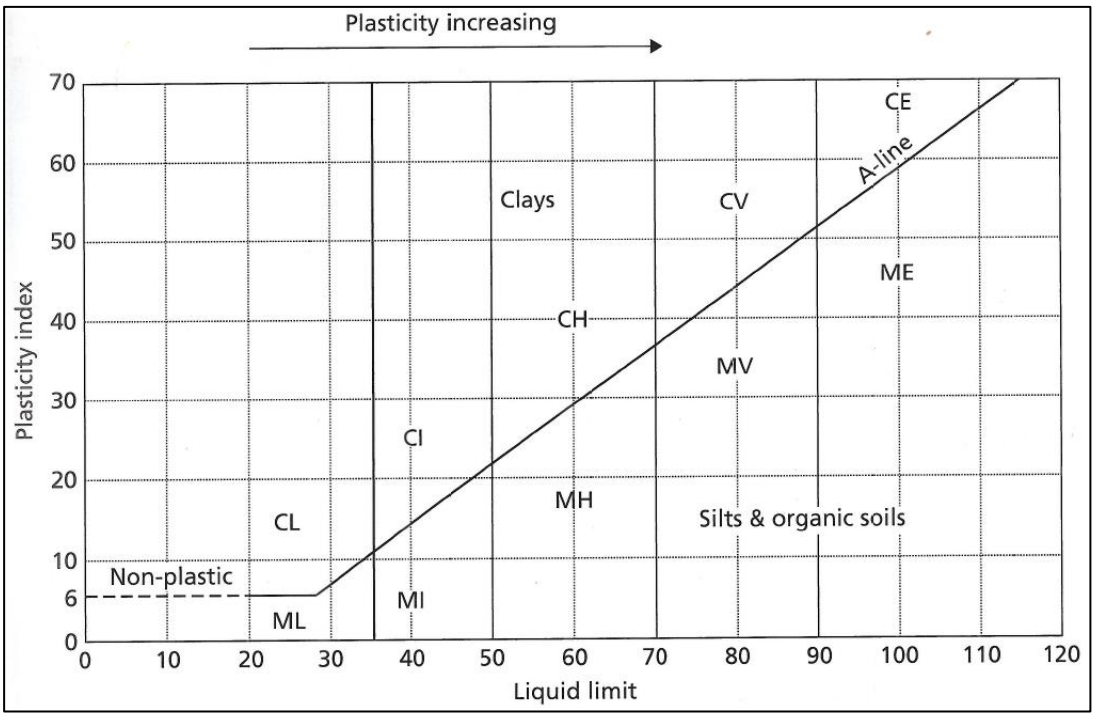

Figure 3-5 - Plasticity chart (Knappett and Craig, 2012)

The test will be done according to the one-point method in A2 from the TMH-1 manual. Mix approximately 50g of the material passing through the 0.425mm sieve with distilled water in a container until it forms a paste. Filled the Casagrande apparatus with the paste until the surface is level. The sample is divided into two parts using a groove apparatus. The Casagrande apparatus is rotated at approximately two blows per second until the contact point between the two halves are 10mm. The number of taps it take to close the groove must be between 22 and 28. A portion on both sides of the contact point is put into a container and weighed to obtain the water content. The following formula is used to calculate the liquid limit. Table 3-1 contains the adjustment factors at the different number of taps to calculate the LL for the soil. (*Standard Methods of Testing Road Construction Materials*. Second, 1986)

$$LL = Moisture\ content \times (\#\ taps \div 25)^{0.12}$$

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Table 3-1 Adjustment factors to calculate the liquid limit from the one-point method.

Number of taps	$(\#\ taps \div 25)^{0.12}$
22	0.985
23	0.990
24	0.995
25	1.000
26	1.005
27	1.009
28	1.014

Method A3 in the TMH-1 manual will be used to determine the PL. Roughly 20g of the paste in the Casagrande apparatus is rolled into threads with a diameter of 3mm without crumbling. The wires are placed in a container and weighed before the sample is dried in an oven at 110°C. The dried sample is removed from the oven to estimate the moisture content differentiation to calculate the PL. The shrinkage limit is determined by using method A4 in the TMH1 manual. A 150mm long container is filled with the paste at the same moisture content as paste used to estimate the LL. The container is dried in the oven at 110°C. The length of the dried sample is measured to calculate the shrinkage percentage. (*Standard Methods of Testing Road Construction Materials*. Second, 1986)

3.6 XRF, XRD and CT scan

The X-Ray Fluorescence (XRF) analysis is used for accurate chemical characterisation of materials. X-Ray Diffraction (XRD) is used to define the crystalline phase or mineral in the samples. The minerals can be identified from the angle of the X-ray that diffract from the sample (*Portable Mineralogy XRD Analyzer*, no date; Sears, Zemansky and Young, 1982; Bortolotti, Pepponi and Lutterotti, 2017). CT scans is a non-destructive method to analyse the microstructure. The processes consist of two parts which the first is the data collection followed by the image reconstruction step. In the data collection step, the sample is photographed with x-ray beams from multiple angles. As different parts of the sample absorb different amounts of the x-ray the photograph show the x-ray penetration pattern. The final step is where is x-ray scans are superimposed to describe the microstructure of the sample in an high quality image (Mokwa, Morris and Lutey, 2011).

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The preparation process is the same for the XRD and XRF analysis. Approximately 40g of the sample is ground into a fine powder in a granite bowl and sent for analysis. The sample for the CT scan is removed with minimal disturbance. A 20mm length of pipe with a diameter of 17mm is cut at a 30º angle. The pipe is pushed into the soil after the experiment is completed and carefully removed with excess soil to keep the sample minimally disturbed. The sample is wrapped in plastic to prevent moisture loss and sent for scanning.

3.7 Scanning electron microscope (SEM)

After the bulk chlorine dioxide experiment is done a 50mm x 50mm x 50mm cube sample is remove and dried in an oven at 110ºC. When all the moisture is removed from the sample it is sent to be scanned. The sample is taken by breaking of a small piece from the centre of the dried cube.

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Chapter 4

4. Results

4.1 XRD and XRF

The Lin vs 2-Theta scale graphs from the XRD analysis were used to identify minerals within the soil. Each spike in the data indicates the presence of a mineral and the value on the 2-Theta scale is used to identify the mineral. The results of the XRD analysis were received as graphs in terms of measurements and phase analysis. The graph in figure 4-1 shows the measurements of the original untreated sample before being treated with chlorine dioxide. The measurements of all three samples after the experiment were plotted on a graph shown in figure 4-2. The measurement of the XRD results for the original and the treated samples are plotted on the graph in figure 4-3. Appendix B show the phase analysis of the original sample and the three treated samples.

The samples were tested in a powder form to obtain the trace element readings in the XRF analysis. Table 4-1 and 4-2 illustrate the comparison between the major and trace elements of the untreated and treated samples. The results of the major elements are shown as a percentage and the trace elements as part per million (ppm).

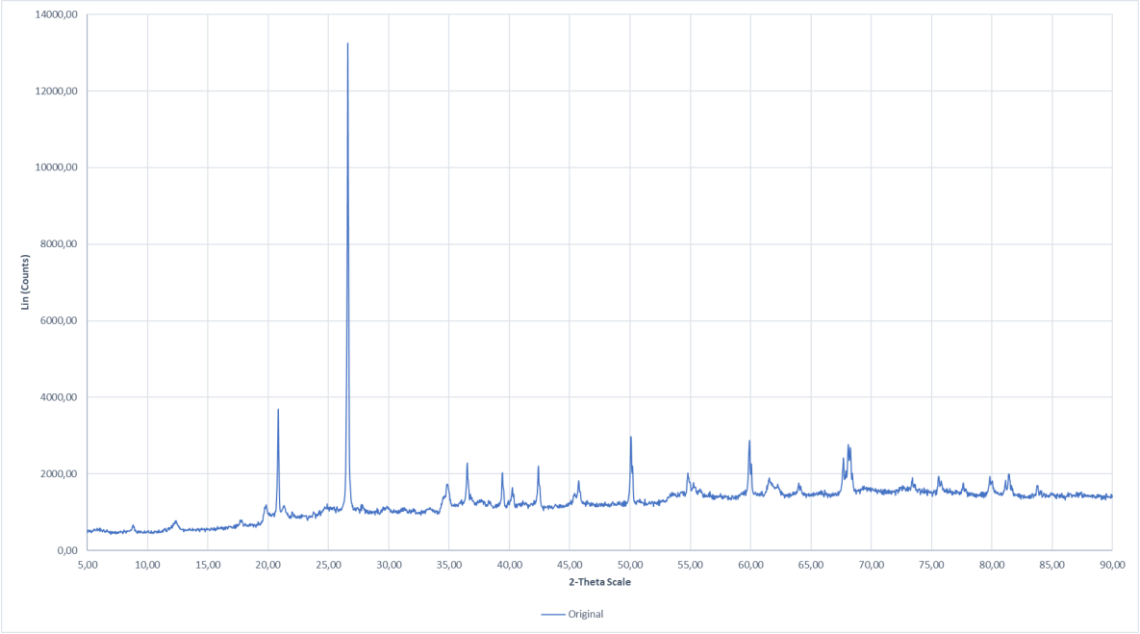

Figure 4-1 Original XRD measurements

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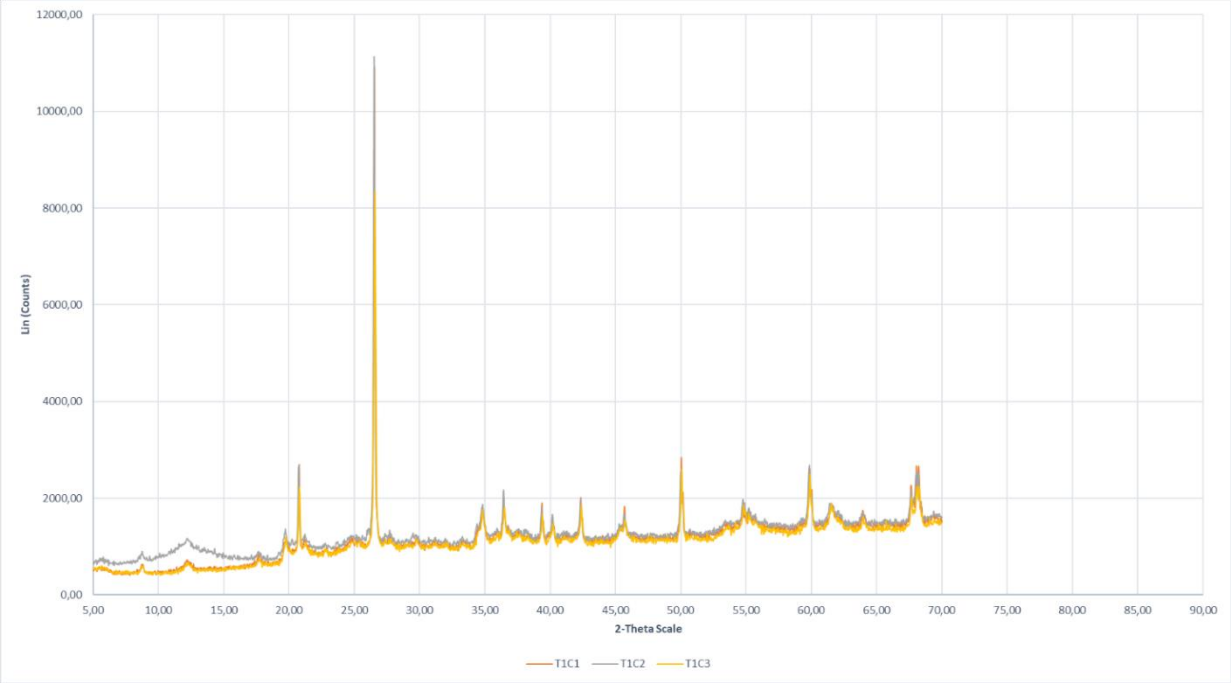

Figure 4-2 XRD measurements of 3 treated samples.

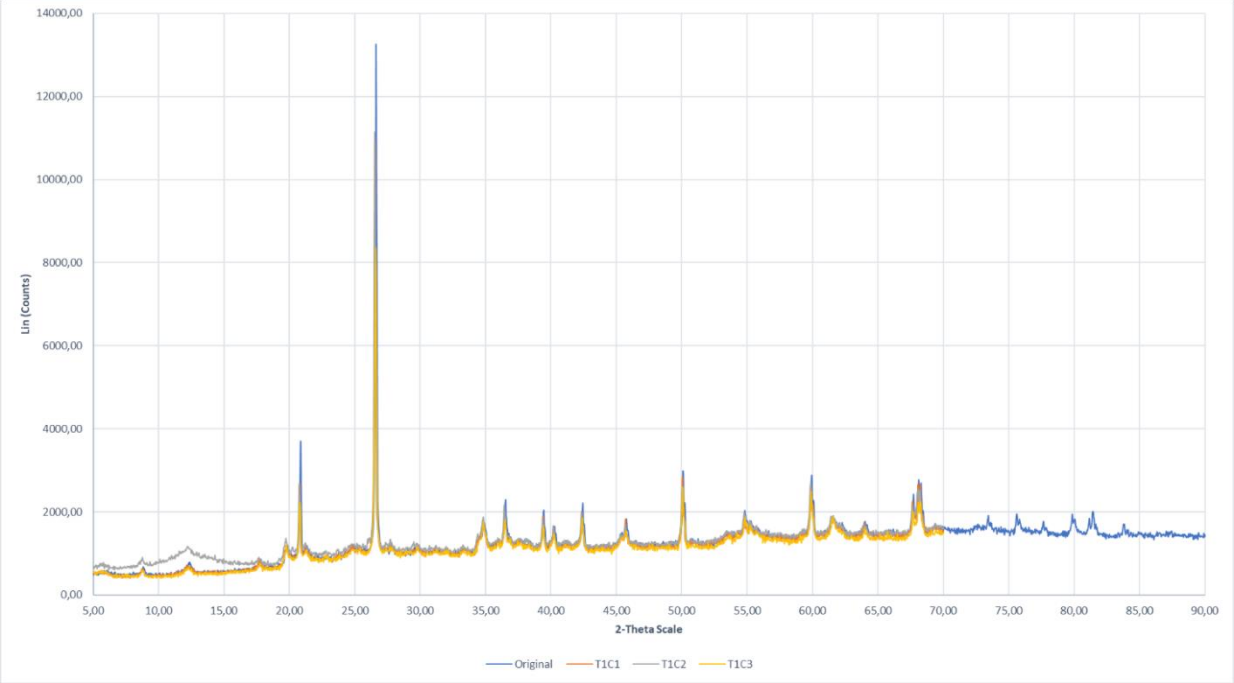

Figure 4-3 All the measurement of the XRD samples

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Table 4-1 Major element from the XRF analysis

Elements	Sample C1 (%)	Sample C2 (%)	Sample C3 (%)	Original sample (%)
Al_2O_3	17.57	18.03	18.05	16.43
CaO	0.31	0.33	0.34	0.46
Cr_2O_3	0.01	0.01	0.01	0.01
Fe_2O_3	8.97	8.62	9.02	9.46
K_2O	2.73	2.87	2.89	2.68
MgO	1.2	1.21	1.25	1.11
MnO	0.09	0.19	0.07	0.11
Na_2O	0.24	0.21	0.22	0.12
P_2O_5	0.05	0.05	0.06	0.06
SiO_2	60.3	59.26	59.12	61.91
TiO_2	0.67	0.68	0.67	0.67
LOI	8.93	8.83	9.03	6.55

Table 4-2 Trace element from the XRF analysis

Elements	Sample C1 (ppm)	Sample C2 (ppm)	Sample C3 (ppm)	Original sample (ppm)
V	149	138	147	123.2
Cr	90	98	96	117.2
Co	33	36	31	21.27
Ni	67	69	58	61.1
Cu	39	29	33	49.8
Zn	102	103	99	86.6
Sr	54	56	53	64.9
Y	54	56	55	41.39
Zr	208	198	196	224.3
Nb	15	16	15	11.6
Ba	876	961	884	1187
Ce	120	131	121	81.4

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Nd	57	61	56	47.6
Pb	24	25	25	27.9
Th	17	15	14	12.57
U	1	10	5	3.37

4.2 Sieve analysis and Hydrometer

The graph in figure 4-4 compares the grading of the first set of experiments with the grading of the untreated sample. The graphs in figure 4-5 show the grading of the experiments contained only clay soil and the untreated samples. Table 4-3 show the percentage coarse sand, fine sand, silt and clay in the soil mortar of each sample. Appendix C shows a table with the sieve analysis results for each sample tested and the table with the hydrometer readings.

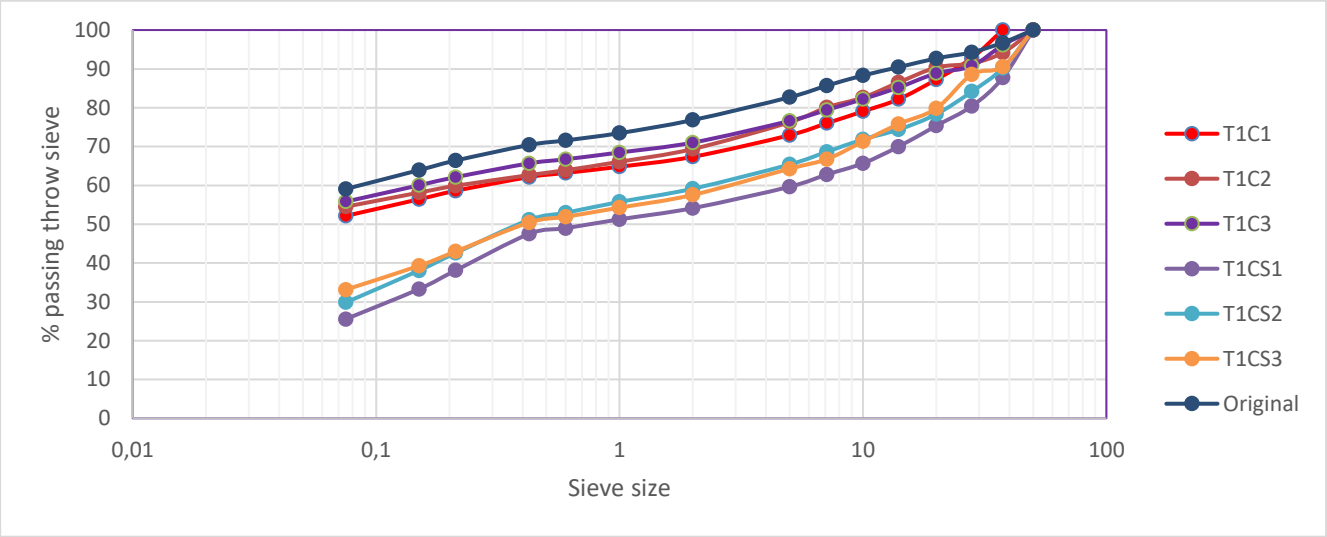

Figure 4-4 Sieve analysis of the original sample and samples with clay soil and clay mixed with coarse grained soil.

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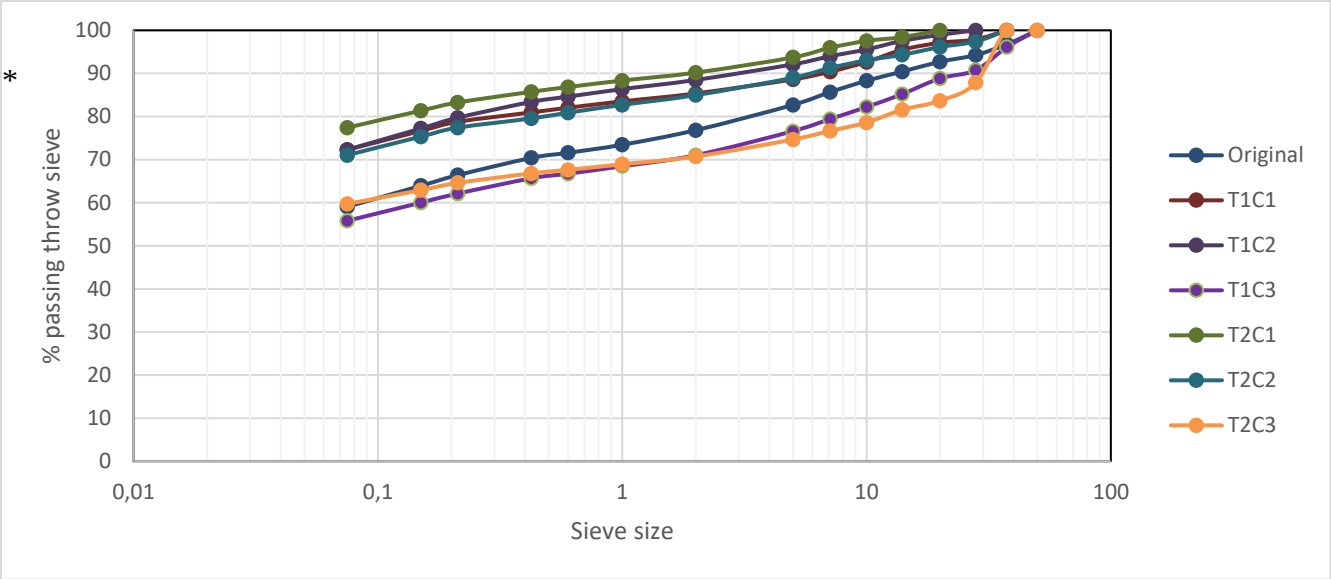

Figure 4-5 Sieve analysis of the clay samples and the original sample

Table 4-3 Percentage coarse sand, fine sand, silt and clay in the soil mortar

	Original	T1C1	T1C2	T1C3	T2C1	T2C2	T2C3	T1CS1	T1CS2	T1CS3
P1	8.36	5.16	5.76	7.55	4.93	6.36	5.56	12.28	13.59	12.37
P2	43.07	43.63	40.52	39.75	43.73	42.14	39.67	60.52	55.3	52.58
P3	21.53	18.97	18.85	18.49	20.91	22.47	28.33	14.91	17.28	14.9
P4	27.3	32.25	34.87	34.21	30.42	29.03	26.44	12.28	13.83	20.16
P5	37.31	43.71	47.53	37.43	46.3	43.76	38.74	14.72	18.4	20.17

4.3 Atterberg limits

The results of the Atterberg test for all the samples are shown in Table 4-4. Figure 4-6 compare the first set of experiments with the untreated sample on the plasticity chart. The clay soil samples treated with chlorine dioxide are compared with the untreated sample on a plasticity chart shown in figure 4-7. Figure 4-8 compare the PI of the samples treated with an ionic surfactant and the untreated sample on a plasticity chart.

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Table 4-4 Atterberg limit results

Liquid Limit (LL)	Units	T1C1	T2C1	T1C2	T2C2	T1C3	T2C3	Original	T1CS1	T1CS2	T1CS3	T2IS1	T2IS2	T2IS3
Holder, wet sample (a)	g	43.8	43.2	41.6	35.4	47.8	36.6	51.8	46.8	50.5	42.1	46.4	44.3	31.4
Holder, dry sample (b)	g	34.9	34.4	33.3	28.6	37.9	29.2	40.9	39.6	42.8	35.2	38.9	37.6	27.6
Mass of holder (c)	g	11.9	12.1	11.9	11.1	12.3	11.5	11.8	11.7	11.7	12.1	19.6	20.6	11.7
Moisture content	%	38.70	39.46	38.79	38.86	38.67	41.81	37.46	25.81	24.76	29.87	38.86	39.41	23.90
Adjustment factor		0.99	1.014	1.000	0.995	0.985	0.99	1.009	0.995	0.985	1.000	0.990	0.995	1.000
Liquid Limit		38.31	40	38.79	38.67	38.10	41.39	37.80	25.68	24.39	29.87	38.47	39.21	23.9
Linear shrinkage														
length of wet sample (a)	mm	150	150	150	150	150	150	150	150	150	150	150	150	150
length of dry sample (b)	mm	138	140	139	142	139	140	141	143	141	143	140	140	140
shrinkage of sample (a-b)	mm	12	10	11	8	11	10	9	7	9	7	10	10	10
Linear shrinkage	%	8	6.67	7.33	5.33	7.33	6.67	6	4.67	6	4.67	6.67	6.67	6.67
Plastic limit (PL)														
Holder, wet sample (a)	g	31.4	28.6	28.3	30.6	37.6	32.3	34.5	33.9	31.2	32.9	30.1	30.4	30.4
Holder, dry sample (b)	g	27.3	25	24.9	26.8	34.2	28.2	30	30.4	28.4	29.5	26.3	26.7	27.8
mass of holder (c)	g	12.1	12	11.8	12.3	20.4	12.1	11.3	11.7	12.6	11.6	11.9	11.9	12
mass of water removed	g	4.1	3.6	3.4	3.8	3.4	4.1	4.5	3.5	2.8	3.4	3.8	3.7	2.6
mass of dry sample	g	15.2	13	13.1	14.5	13.8	16.1	18.7	18.7	15.8	17.9	14.4	14.8	15.8
Plastic Limit	%	26.97	27.69	25.95	26.21	24.64	25.47	24.06	18.72	17.72	18.99	26.39	25	16.46
Plasticity index (LL - PL)		11.72	11.77	12.83	12.65	14.03	16.34	13.39	7.09	7.04	10.88	12.47	14.41	7.44

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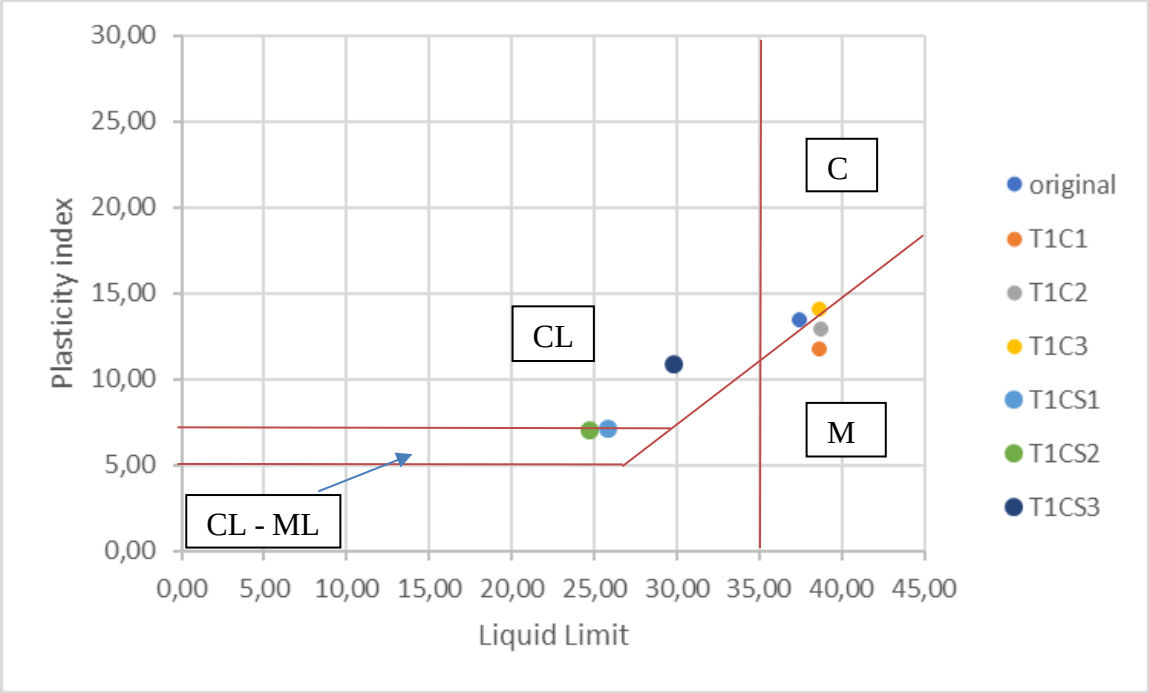

Figure 4-6 Plasticity chart for the first set of experiments

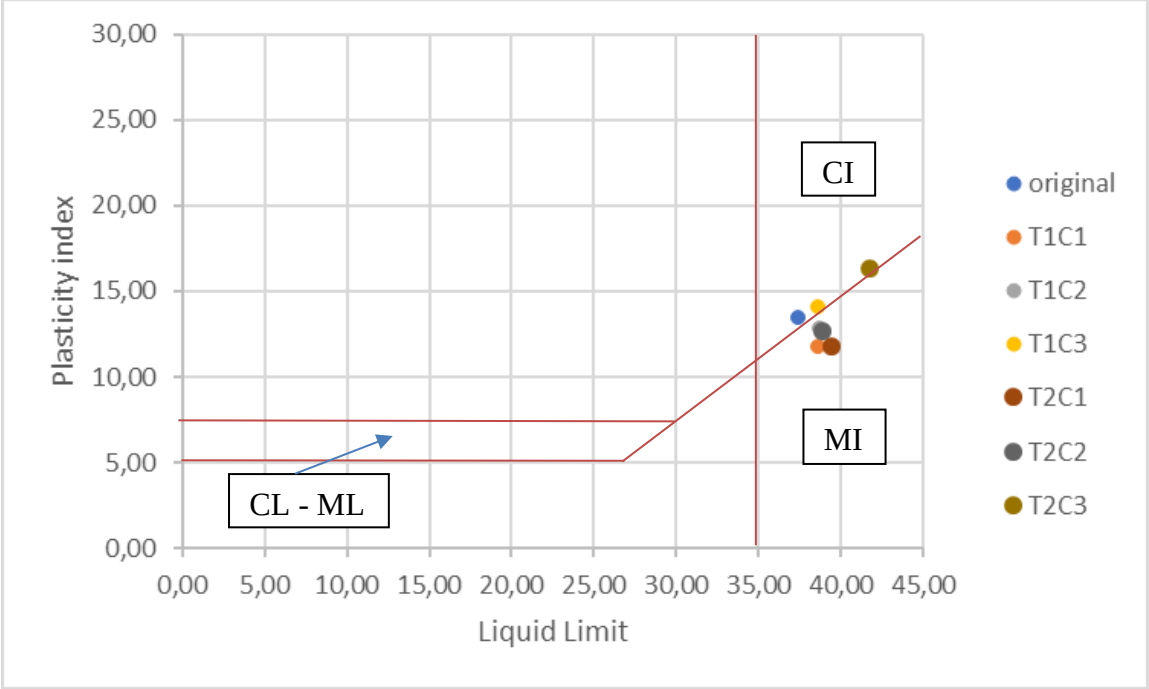

Figure 4-7 Plasticity chart of the clay sample and the original sample

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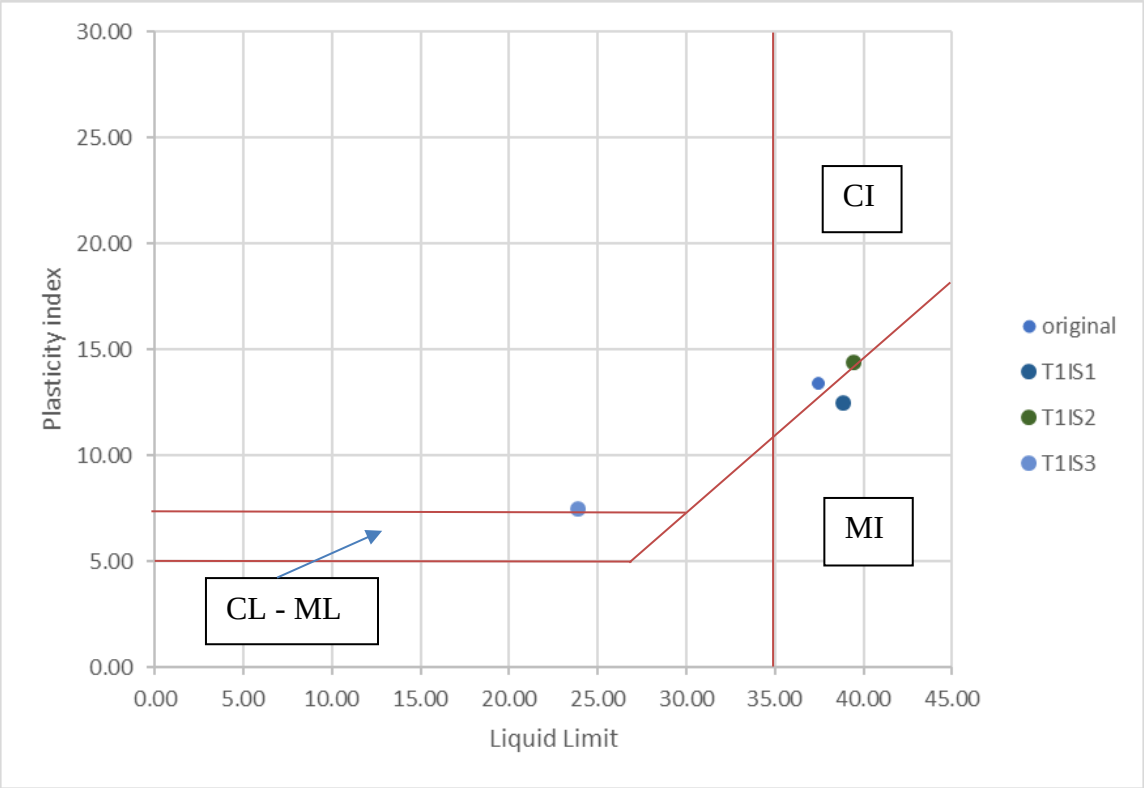

Figure 4-8 Plasticity chart of the original and samples treated with an ionic surfactant

4.4 CT scan

The CT scan results were analysed with the difference in density. The different shades of grey indicate different densities and black shows a void. Figure 4-9 compares the CT scan results of the untreated sample on the left with the treated sample T2C2 on the right.

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Original sample Treated sample

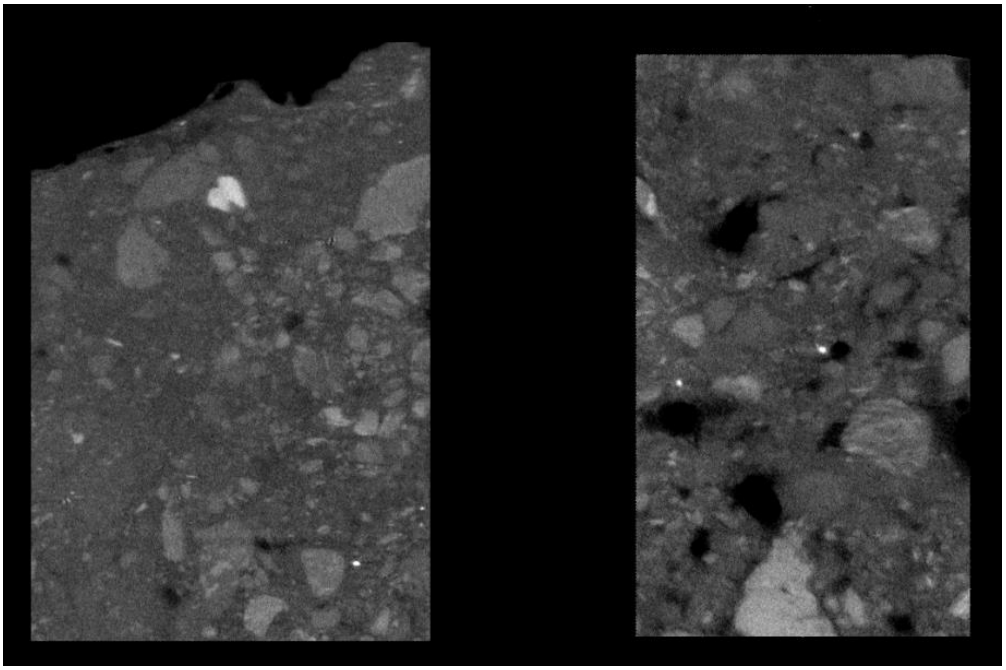

Figure 4-9 CT scan of the original untreated sample and treated sample T2C2

4.5 SEM

4.5.1 Visual comparison

The SEM is used to compare the particle of the soil before and after the treatment. Figures 4-10 to 4-17 show the comparison of the soil structure between the untreated sample and the sample treated with chlorine dioxide at different magnifications. Figures on the left are untreated and the figures on the right have been treated with chlorine dioxide. The particles coalesce into flocculated layers after the chlorine dioxide treatment.

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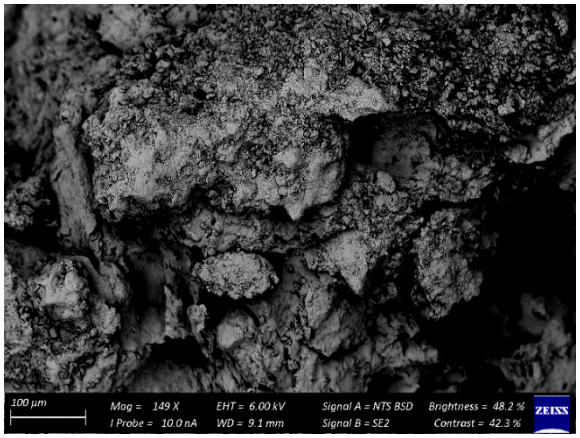

Figure 4-10 Untreated sample magnified at 149x

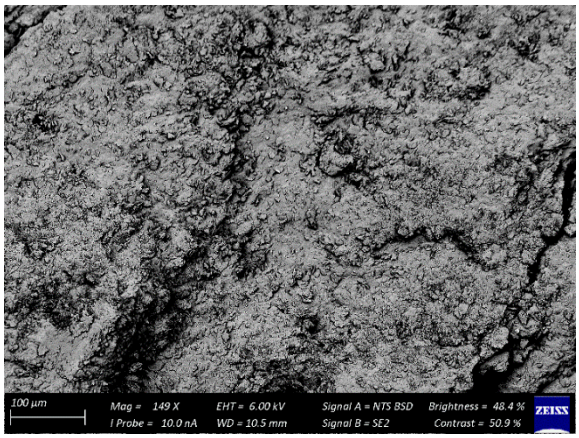

Figure 4-11 Treated sample magnified at 149x

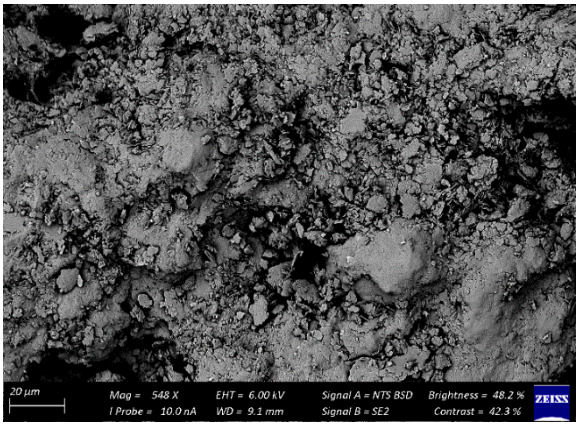

Figure 4-12 Untreated sample magnified at 548x

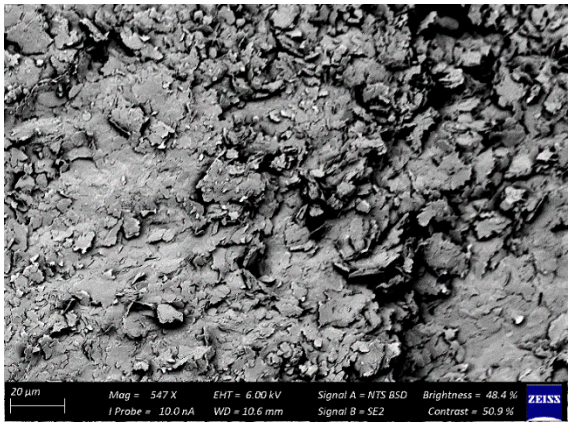

Figure 4-13 Treated sample magnified at 547x

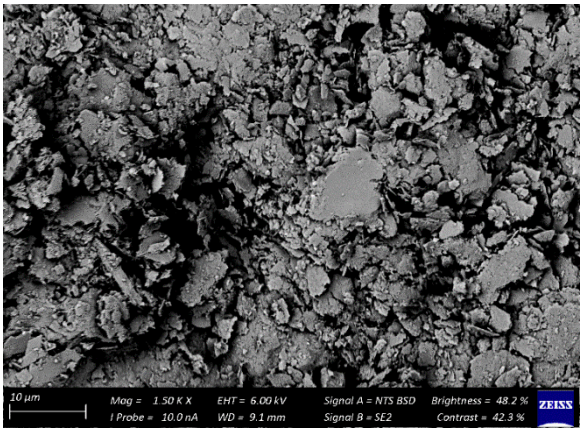

Figure 4-14 Untreated sample magnified at 1500x

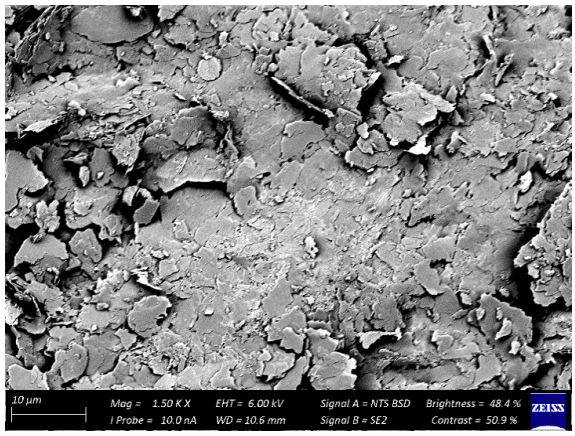

Figure 4-15 Treated sample magnified at 1500x

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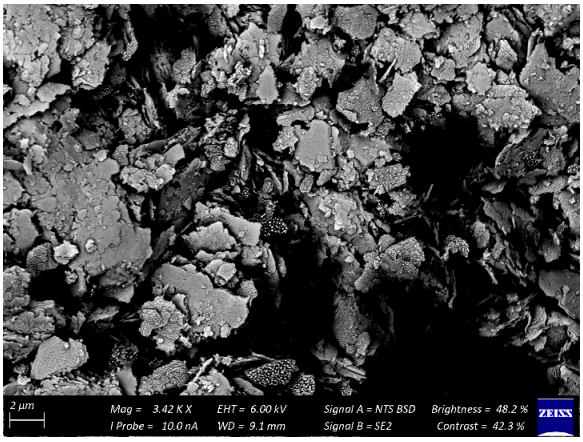

Figure 4-16 Untreated sample magnified at 3420x

Figure 4-17 Treated sample magnified at 3440x

4.5.2 Consistency of the soil structure

Figures 4-18 and 4-19 compare the soil structure of the untreated sample at different locations with approximately the same magnification. Figures 4-20 and 4-21 compare the soil structure of the treated sample at different locations with approximately the same magnification. The figure of the soil structure confirms the structure is consistent throughout the sample.

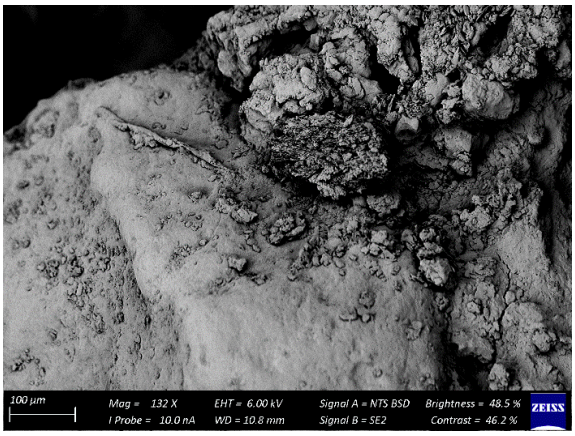

Figure 4-18 Untreated sample magnified at 132x

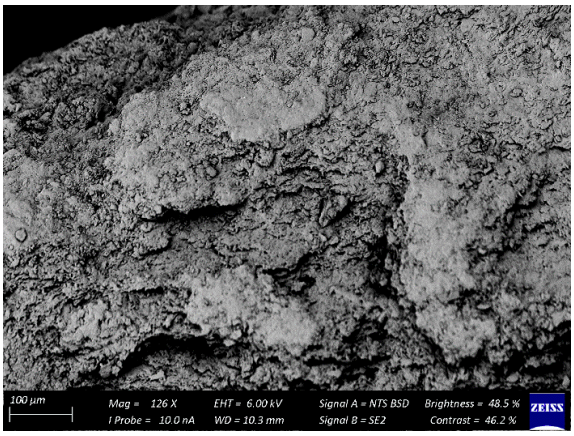

Figure 4-19 Untreated sample magnified at 126x

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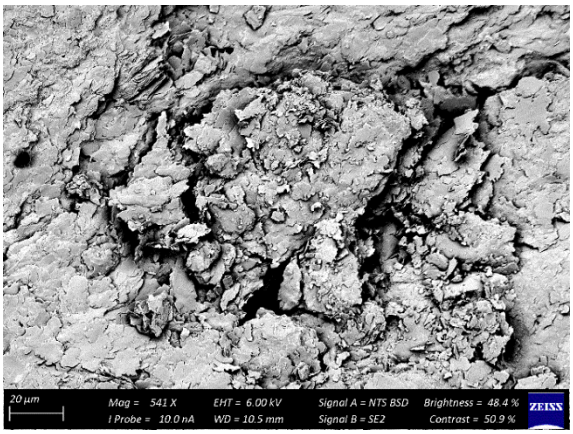

Figure 4-20 Treated sample magnified at 541x

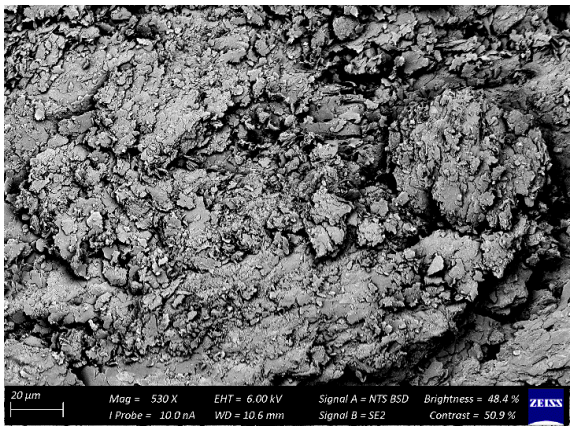

Figure 4-21 Treated sample magnified at 530x

4.6 Permeability

The following variables remained constant for both the untreated and treated sample: Area and height of the samples is 17671.41 mm^2 by 130 mm and the cross-section area of the manometer is 6.9 mm^2. Table 4-5 show the reference heights used in the tests. Table 4-6 and 4-7 show the results of the permeability test for the untreated samples. The permeability results of the chlorine dioxide treated sample is shown in table 4-8 and 4-9. The tests were done at 18ºC and Table 4-10 shows the final permeability results after the temperature correction is made.

Table 4-5 Reference data for permeability test

Reference point	Height above datum (mm)	Height above outlet (mm)
h_0	375	-
h_1	1850	1475
h_2	1900	1525
h_3	1950	1575

Table 4-6 Permeability of the first untreated sample

Reference point	Time		Height ratio	$k_T\ (m/s)$
3 - 2	7-12	7.2	$\frac{1575}{1525} = 1.03$	3.48×10^{-9}
2 - 1	6-50	6.83	$\frac{1525}{1475} = 1.03$	3.66×10^{-9}

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Table 4-7 Permeability of the second untreated sample

Reference point	Time		Height ratio	$k_T\ (m/s)$
3 - 2	7-28	7.47	$\frac{1575}{1525} = 1.03$	3.35×10^{-9}
2 - 1	7-08	7.13	$\frac{1525}{1475} = 1.03$	3.51×10^{-9}

Table 4-8 Permeability of first sample treated with chlorine dioxide

Reference point	Time		Height ratio	$k_T\ (m/s)$
3 - 2	0-44	0.73	$\frac{1575}{1525} = 1.03$	3.43×10^{-8}
2 - 1	0-42	0.7	$\frac{1525}{1475} = 1.03$	3.57×10^{-8}

Table 4-9 Permeability of second sample treated with chlorine dioxide

Reference point	Time		Height ratio	$k_T\ (m/s)$
3 - 2	0-52	0.87	$\frac{1575}{1525} = 1.03$	2.88×10^{-8}
2 - 1	0-49	0.82	$\frac{1525}{1475} = 1.03$	3.05×10^{-8}

Table 4-10 Temperature correction to the permeability results

Sample	Average k_T	Temperature (ºC)	Correction factor	$k_{20}\ (m/s)$
Untreated	3.5675×10^{-9}	18	1.06	3.78×10^{-9}
Untreated	3.43×10^{-9}	18	1.06	3.64×10^{-9}
Treated	3.5×10^{-8}	18	1.06	3.71×10^{-8}
Treated	2.97×10^{-8}	18	1.06	3.14×10^{-8}

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4.7 Organic matter

Based on previous results it can be postulated that the chlorine dioxide reacts with the organic matter to increase the voids in the sample. The chlorine can possibly react with the organic matter, as a result voids can form. The sample is burnt at 600ºC in a kiln to remove all organic matter. Table 4-11 shows the weight of the untreated and treated samples at 40ºC and at 600ºC. The reduction in the mass is given in grams and as a percentage. Figure 4-22 and 4-23 show the soil structure of the untreated sample after being heated to 40 °C and 600 °C.

Table 4-11 Amount of organic matter

Sample	Untreated		Treated	
	1	2	1	2
Mass at 40ºC (g)	19.9	20.5	13	16.6
Mass at 600ºC (g)	18.6	19	11.8	16.1
Mass reduction (g)	1.3	1.5	1.2	0.5
Mass reduction (%)	6.53	7.32	9.23	3.01

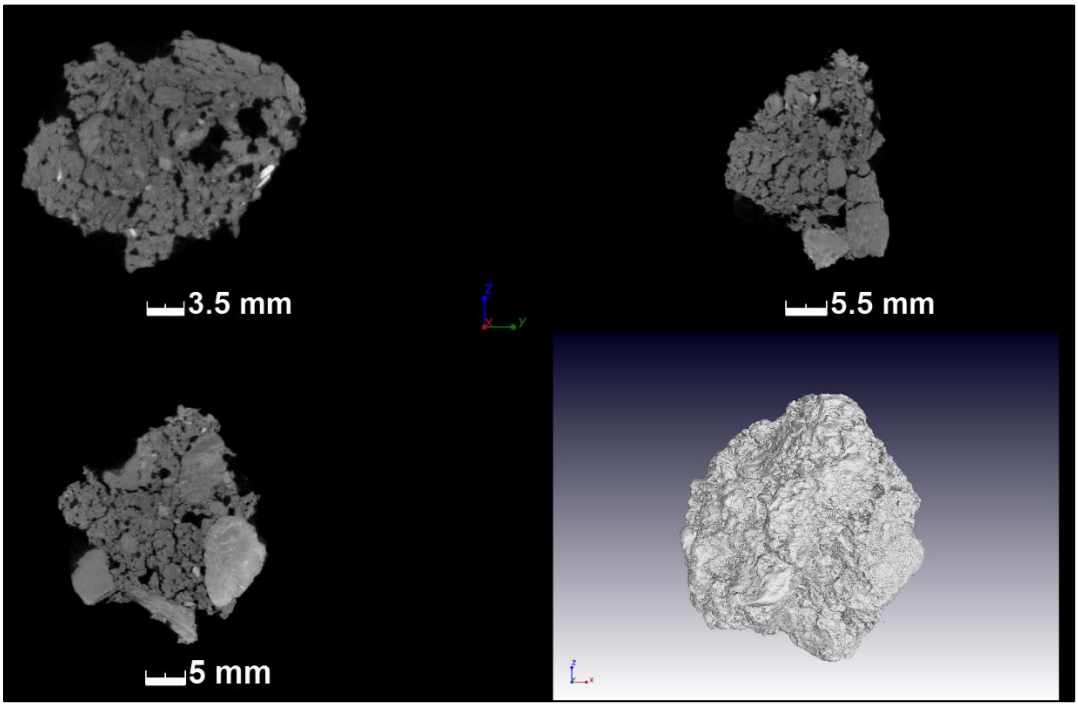

Figure 4-22 Soil structure of untreated sample at 40 °C

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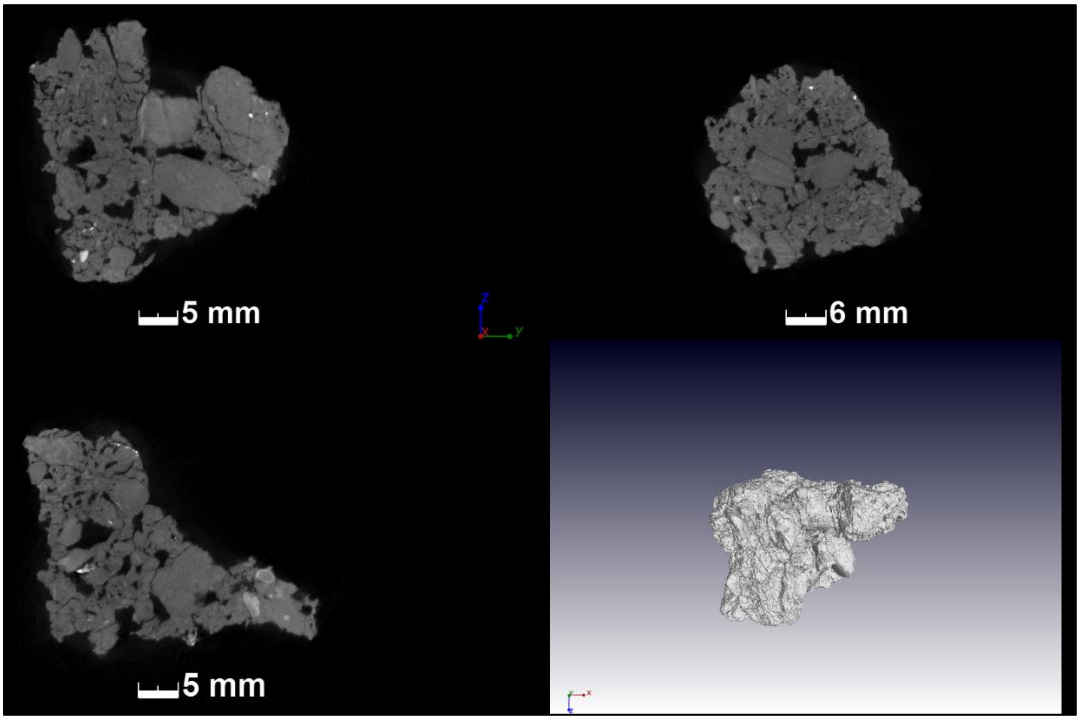

Figure 4-23 Soil structure of untreated sample at 600 °C

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Chapter 5

5. Interpretation of the results

5.1 Mineralogy

The aim of this study was to compare the mineralogy of the untreated and treated sample to identify any difference. The soil structure and permeability will then be compared for possible changes.

The soil contains high amounts of quartz. Clay minerals are the same before and after the experiment. There is more Muscovite present in the soil than Kaolinite where the Muscovite is more active than the Kaolinite. The mineralogy of the soil is not affected by the treatment as can be seen in figure 4-3. Sample T1C2 showed a difference from 5 to 18 on the 2-Theta scale because of a possible metamorphoses in the mineral. This difference is not considered as a change in mineralogy, because the results of the other two experiments are similar to the untreated sample.

There was a slight increase in the following major elements Al_2O_3, Na_2O and the loss on ignition. The following major elements decreased after the treatment: Fe_2O_3 and SiO_2. These trace elements increased after the treatment: *V*, *Co*, *Zn*, *Y*, *Ce*. The following trace elements decreased after the treatment: *Cr*, *Cu*, *Sr*, *Zr*, *Ba*. The changes are not significant therefore it is not considered as a change in the elements.

5.2 Particle sizes

The first set of experiments indicated the particle size increased in the clay-sand mixture experiment. By comparing the particle size distribution of the clay soil and the clay-sand mixture experiments all the samples in the clay-sand experiment and sample T1C3 showed an increase in particle size after the chlorine dioxide treatment. Samples T1C1 and T1C2 showed a decrease in particle size after being treated with chlorine dioxide. The clay-sand mixture experiment must show an increase in particle size, because the particle size of course grained soil is larger than a clay soil. Therefore, the second set of experiments was done with clay soil and not with the clay-sand mixture.

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The second set of experiments confirm the results of the first set as the change in particle size remained constant. The change in particle size distribution curve is possibly clods and therefore chlorine dioxide cannot be used to change the particle sizes of clay soil. The hydrometer calculations show that the coarse and fine sand increase after the treatment for the clay and coarse grained soil samples. These results are from the added coarse grained soil. The clay soil only experiments show an increase in clay after the chlorine dioxide treatment.

The course grained soil had a significant influence on the Atterberg limits results. The LL, PL and linear shrinkage for the clay-sand experiment is lower than the untreated sample, because course grained soil has no plasticity. There was a slight increase in the linear shrinkage of the clay samples after the treatment. The LL and PL increased for all the clay soil sample after the experiment by using the formulas in table 4-2. Samples 1 and 2 had a lower PI than the untreated sample and sample 3 has a higher PI than the untreated sample. These changes imply that samples 1 and 2 are less active and sample 3 is more active than the untreated sample. The results of the ionic surfactant are not consistent with the chlorine dioxide tests therefore chlorine dioxide does not react as an ionic surfactant.

5.3 Soil structure

After the results of the sieve analysis verified that there is a small change in particle size, a CT scan was done to compare the soil structure before and after treatment. Figure 4-10 shows the voids increase after the soil is treated with chlorine dioxide. The CT scan of the soil structure after the organic matter is burnt away does not show a significant difference in voids. A falling head permeability test was completed to determine if the increase in porosity would impact the permeability. The average permeability at 20ºC increased from $3.71 \times 10^{-9}\ m/s$ to $3.43 \times 10^{-8}\ m/s$ after the chlorine dioxide treatment. The SEM results show that the clay particles coalesce into flocculated layers, but the voids as seen in the CT scan is not visible in the SEM photographs. The untreated and treated material was burnt at 600ºC to remove all the organic matter. After the samples had been burned, their weight was be taken to estimate how much organic matter was present. The change in the amount of organic matter present in the untreated and treated samples was not consistent.

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Chapter 6

6. Conclusion and Recommendations

6.1 Conclusion

The chlorine dioxide had no effect on the mineralogy of the soil. This chemical cannot be used to reduce the shrink and swell behaviour of clay soils. The treatment with the 11.25ml/l chlorine dioxide showed an increase in particle size where in the other two experiments the particle sizes decreased after the treatment. The overall change in particle sizes is not sufficient to confirm that chlorine dioxide can be used to change the particle size distribution of clay soil. The clay soil samples showed an increase in clay after the chlorine dioxide experiment. This result can be from a reaction between the chlorine dioxide and the clay particles. Chlorine dioxide should not be used at a concentration of 11.25ml/l, because the plasticity of the soil increased after the treatment.

The CT scan of the saturated soil sample showed the voids increased after the soil was treated with chlorine dioxide. The chemical does not affect the organic matter within the soil. Therefore, the conclusion can be made that the increase in voids are not from a reaction between the chlorine dioxide and the organic matter. Chlorine dioxide coalesce the soil structure into flocculated layers, but the increase in voids is not visible on the scans from the SEM. The permeability of the soil increased after the treatment. Therefore, the chlorine dioxide did not change the mineralogy of the soil, but the permeability of the soil increased.

6.2 Recommendations

- Alternative methods must be researched to introduce the chlorine dioxide into the soil where there is no irrigation system in use.
- More accurate mineralogy analysis can be done by extracting the clay minerals before the XRD analysis is done according to Prof. C. Clarke (C Clarke 2019, personal communication, 6 May).
- More consistent results can be gathered for the soil structure tests by using more samples.
- The permeability test must be repeated with compaction at different moisture contents.
- Further research is needed into the uses of chlorine dioxide in soil for geotechnical purposes.

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References

‘Alternative Disinfectants and Oxidants Guidance Manual’ (1999) *USEPA, 1999. EPA Guidance Manual Alternative Disinfectants and Oxidants*. doi: 815-R-99-014.

Bortolotti, M., Pepponi, G. and Lutterotti, L. (2017) ‘Combining XRD and XRF analysis in one Rietveld-like fitting’, *Powder Diffraction*.

Dixon, J. B., Weed, S. B. and Dinauer, R. C. (eds) (1989) *Minerals in Soil Environments*. first. Soil Science Society of America.

Elarabi, H. (2015) ‘Factors Influencing Swelling Behaviour of Expansive Soil’, *Building and Road Research*, (December 2004).

Head, K. H. (no date) *Manual of Soil Laboratory Testing*. London: Pentech Press.

Holtz, R. D., Kovacs, W. D. and Sheahan, T. C. (2011) *An Introduction to Geotechnical Engineering*. second. Pearson.

Huang, C. *et al.* (2019) ‘Factors Affecting the Swelling-Compression Characteristics of Clays in Yichang, China’, *Advances in Civil Engineering*.

Kaolinite (no date). Available at: https://mineralseducationcoalition.org/minerals-database/kaolinite/ (Accessed: 30 April 1BC).

King, H. M. (no date) *Expansive Soil and Expansive Clay*. Available at: https://geology.com/articles/expansive-soil.shtml.

Knappett, J. A. and Craig, R. F. (2012) *Craig’s soil mechanics*. Eighth. New York: Spon Press.

Lemon, K. (2013) *Hydrometers- A Guide to applications and usage*. Available at: https://camblab.info/wp/index.php/hydrometers-a-guide-to-applications-and-usage/ (Accessed: 21 April 2019).

Stellenbosch University https://scholar.sun.ac.za

Long, B. W., Hulsey, R. A. and Hoehn, R. C. (2010) 'Ozone : Science & Engineering Complementary uses of chlorine dioxide and ozone for drinking water treatment', *Ozone: Science & Engineering*, 21, pp. 465–476. doi: 10.1080/01919512.1999.10382885.

Marini, L. (2007) *Geological Sequestration of Carbon Dioxide*. first. Elsevier.

Mason John, Kielman Gary, D. M. (1999) 'Chlorine Dioxide chemistry', p. 6.

Mitchell, J. K. (1993) *Fundamentals of soil behavior*. second. New York: John Wiley & Sons.

Mitchell, P. W. (2013) 'Climate Change Effects on Expansive Soil Movements', *International Conference of Soil Mechanics and Geotechnical Engineering*, 18.

Mokhtari, M. and Dehghani, M. (2012) 'Swell-Shrink Behavior of Expansive Soils, Damage and Control', *The Electronic Journal of Geotechnical Engineering*, 17, p. 2673–2682. Available at: http://www.surevoid.com/...,.

Mokwa, R. L., Morris, Z. L. and Lutey, W. A. (2011) 'X-Ray computed tomography: A new pedagogical tool for studying micro and macro geomaterial properties', *American Society for Engineering Education*. doi: 10.13140/RG.2.1.1827.1846.

Nelson, J. D. and Miller, D. J. (1992) *Expansive soils*. New York: John Wiley & Sons.

Portable Mineralogy XRD Analyzer (no date). Available at: https://www.911metallurgist.com/equipment/portable-xrd-analyzer/ (Accessed: 21 April 2019).

Sears, F. W., Zemansky, M. W. and Young, H. D. (1982) *University Physics*. sixth. Addison-Wesley.

Springman, S. and Davison, L. (2000) *Soil description and classification, University of the West of England*. Available at: https://environment.uwe.ac.uk/geocal/SoilMech/classification/soilclas.htm.

Sridharan, A. and Jayadeva, M. S. (1982) 'Double layer theory and compressibility of clays', *Géotechnique*, 32.

Standard Methods of Testing Road Construction Materials. Second (1986). Pretoria. Available at:

Stellenbosch University https://scholar.sun.ac.za

http://asphalt.csir.co.za/tmh/.

Suchfield, G. A. (1991) ‘United States Patent (19)’, *United States Patent*.

Vayne, S. and Harrison, J. (eds) (2000) *Rocks and Minerals*.

Wu, M. *et al.* (2012) ‘Characterization of chlorine dioxide as disinfectant for the removal of low concentration microcystins’, *Frontiers of Environmental Science & Engineering*, 6(1), pp. 75–81. doi: 10.1007/s11783-011-0331-5.

Wu, M. S. and Xu, X. (2019) ‘Inactivation of antibiotic-resistant bacteria by chlorine dioxide in soil and shifts in community composition’, *Royal Society of Chemistry Advances*, (12).

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Appendix A

US Government registration

1. EPA bacterial and fungicidal registrations for hard, non-porous surfaces in hospitals, laboratories and medical environments.
2. EPA bacterial and fungicidal registration for instruments in hospital and dental environments
3. EPA registration as a dental pumice disinfectant.
4. EPA registration for a terminal sanitising rinse for food contact surfaces in food processing plants, such as poultry, fish, meat, dairies, bottling plants, breweries and restaurants.
5. EPA registration for disinfections of environmental surfaces such as floors, walls and ceilings in food processing plants, such as poultry, fish, meant, diaries, bottling plants, breweries and restaurants.
6. EPA registration for sanitising rinse of uncut/t, peeled fruits and vegetables at 5ppm followed by a potable water rinse.
7. EPA registration for disinfections of water systems found aboard aircraft, boats, mobile vehicles, offshore drillings rigs, etc.
8. EPA registration for treatment of stored potable water, at 5ppm, for drinking water.
9. EPA registration for general disinfection and deodorization of ventilation systems and air conditioning ductwork.

FDA

1. Approved compound in food processing plants for all food contact surfaces.

USDA

1. P- 1 approval for bacterial and mould control in federally inspected meat and poultry processing plants for environmental surfaces.
2. D – 2 approval as terminal sanitising rinse not requiring a water flush on all food surfaces found in food processing plants.
3. D – 3 approvals as a substance for washing fruit and vegetables that are used as ingredients of meat, poultry, and rabbit products.

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4. G – 5 approvals for treatment of cooling and retort water in official establishments operating under the Federal meat and poultry product inspection program.

The United Kingdom Drinking Water Inspectorate

1. Approved under the Water Act 1989, for the introduction into water, which is to be supplied for drinking, washing, cooking, or food production purposes. On condition that the combined concentration of chlorine dioxide, chlorite and chlorate does not exceed 0.5mg/litre as chlorine dioxide in the water entering the supply.
2. List of Substances, Products and Processes approved under Regulations 25 and 26 for use as a disinfectant for water works apparatus, distribution pipes and service reservoirs, on condition that it is used in accordance with the approved Water Systems Disinfection Manual. Chlorine Dioxide is the only product other than chlorine to have gained this approval.
3. Approved under the Water (Scotland) Act 1980, part VI A. Water Supply (water quality) (Scotland) Regulations 1990. Water Supply (Water Quality) (Scotland) Amendment Regulations 1991, on the same terms and conditions as set out above.

The United Kingdom Ministry of Agriculture, Fisheries and Foods

1. Approved for use as a disinfectant for all purposes of the Animal Health Act 1981 and in respect of: - Foot & Mouth Disease of Poultry Orders: Swine Vesicular Disease Orders: Tuberculosis Orders: General Orders made under the Animal Health Act 1981.

Australian Regulations

1. Clearance received from the National Registration Authority for Agricultural and Veterinary Chemicals.
2. Approved under the Commonwealth Export Control Act 1982 under Category 6 for use as a terminal Sanitising Rinse, no rinse required when used in accordance with manufacturer’s directions.

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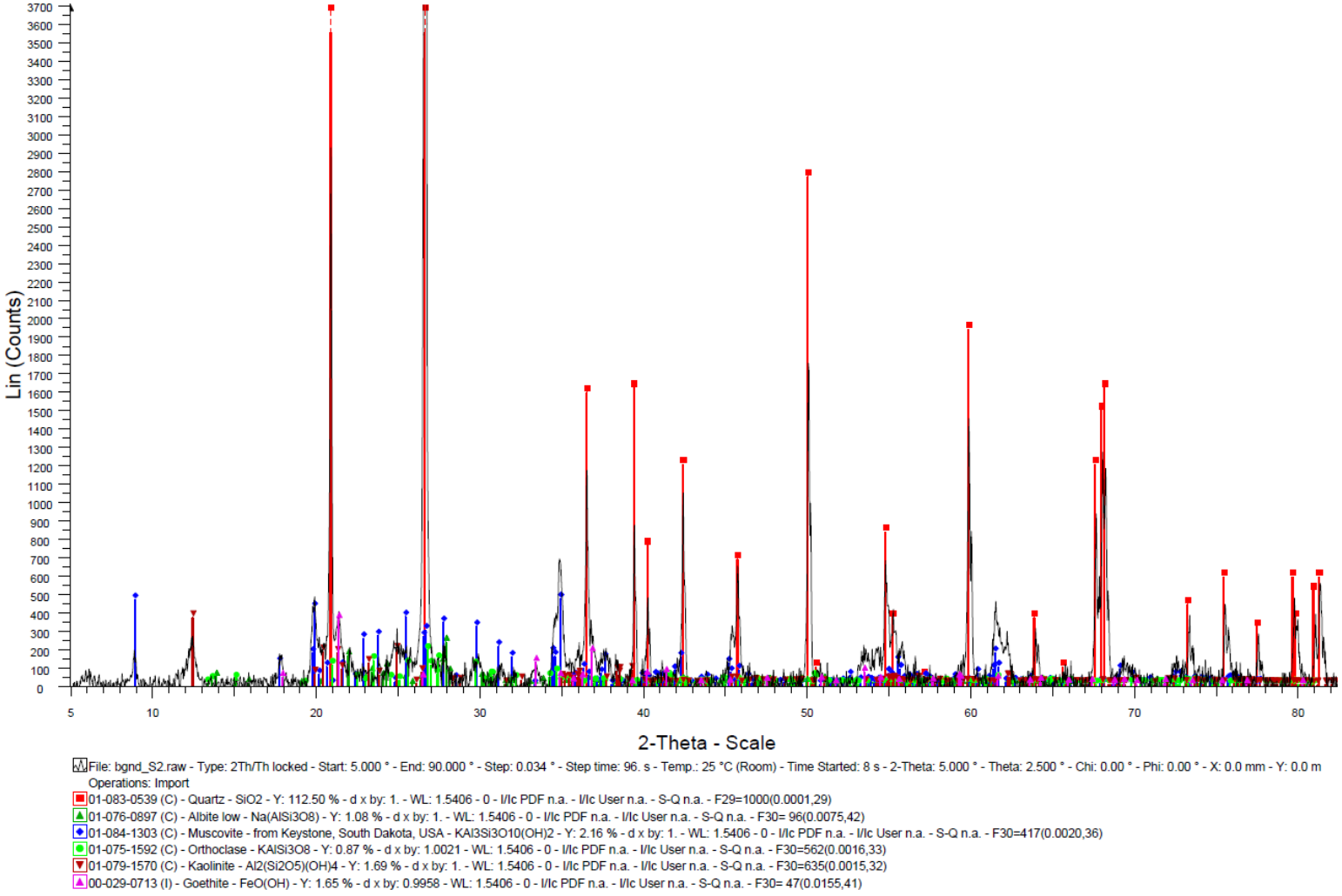
Appendix B

Phase analysis of the original sample



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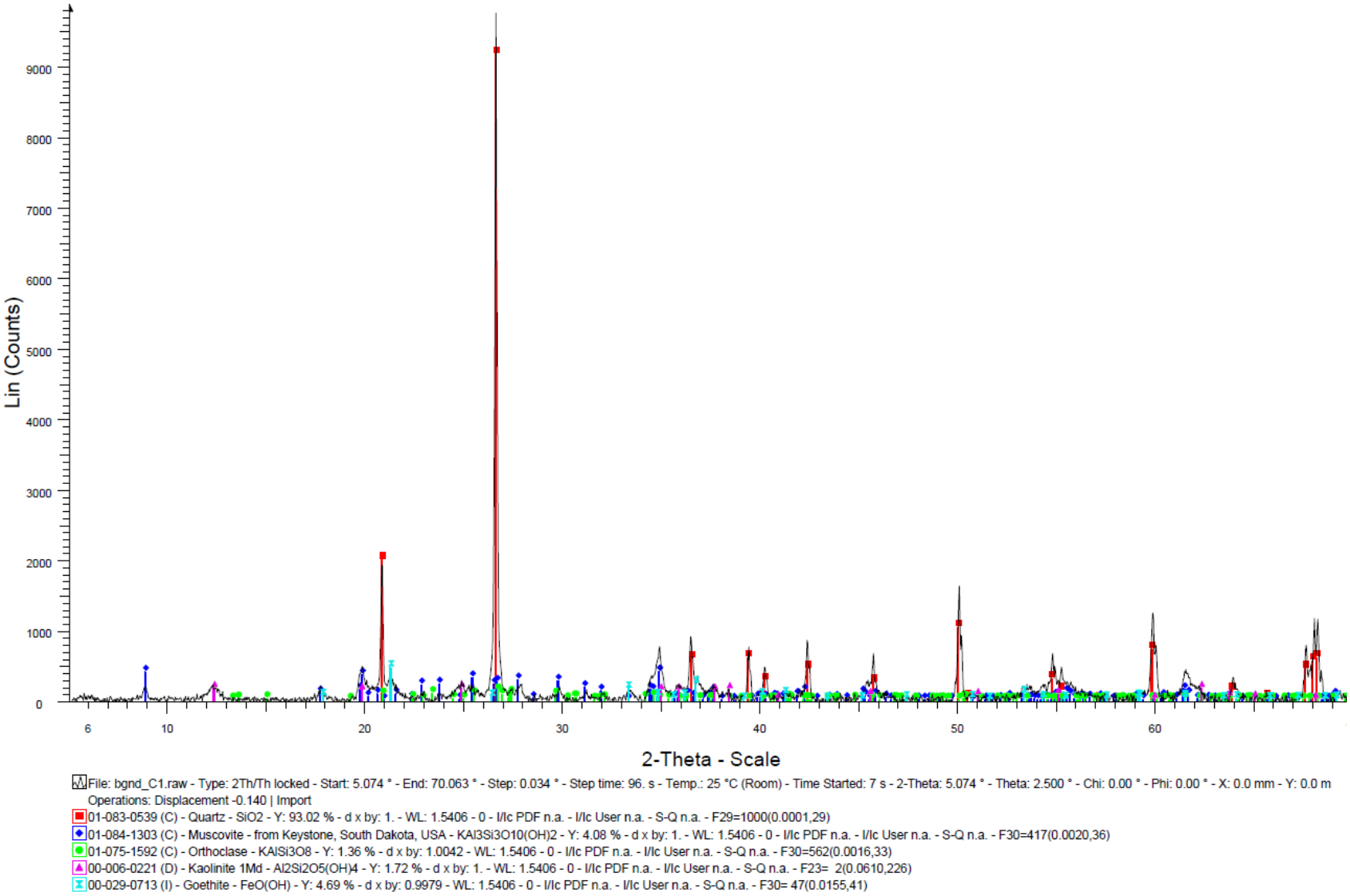
Phase analysis of the sample with concentration of 3.75ml/L



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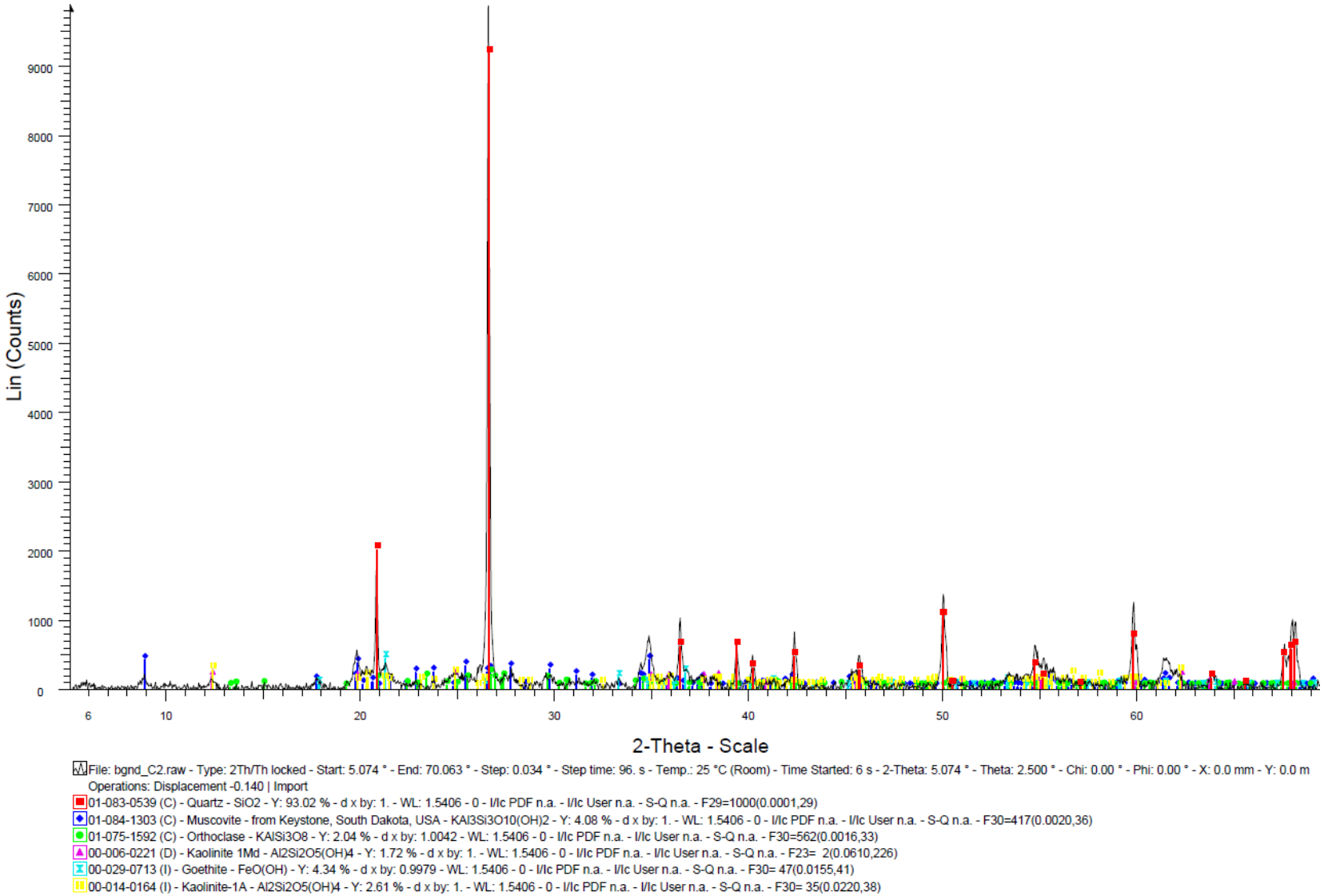
Phase analysis of the sample with concentration of 7.5ml/L



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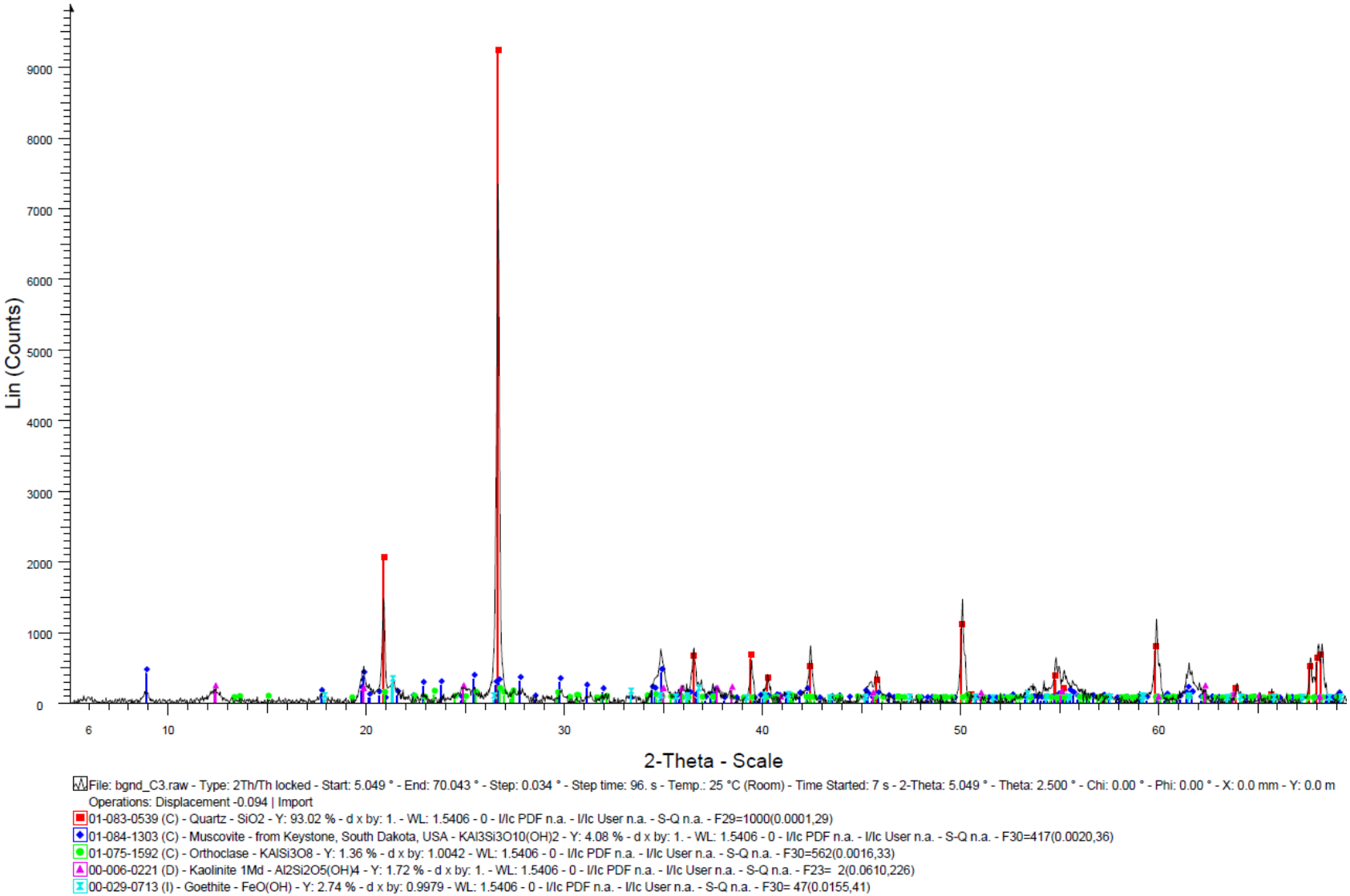
Phase analysis of the sample with concentration of 11.25ml/L



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Appendix C

Original sample:

Sieve analysis of the original sample

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	65	65	3,25	96,75
28	49,5	114,5	2,475	94,275
20	31,5	146	1,575	92,7
14	45,5	191,5	2,275	90,425
10	42,5	234	2,125	88,3
7,1	52,5	286,5	2,625	85,675
5	59,5	346	2,975	82,7
2	117,5	463,5	5,875	76,825
1	67,5	531	3,375	73,45
0,6	37,5	568,5	1,875	71,575
0,425	23,5	592	1,175	70,4
0,212	80,26	672,26	4,01	66,39
0,15	49,28	721,54	2,46	63,92
0,075	97,15	818,69	4,86	59,07
0,075>	1181,31	2000	59,07	0

Hydrometer sieve analysis for original sample

Sieve Size (mm)	Fraction passing %
0,212	94,3
0,15	90,8
0,075	83,9

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Sample T1C1:

Sieve analysis of sample T1C1

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	0	0	0	100
28	42,3	42,3	2,115	97,885
20	15,6	57,9	0,78	97,105
14	32,6	90,5	1,63	95,475
10	56,4	146,9	2,82	92,655
7,1	44,9	191,8	2,245	90,41
5	35,9	227,7	1,795	88,615
2	65,2	292,9	3,26	85,355
1	36,7	329,6	1,835	83,52
0,6	29,7	359,3	1,485	82,035
0,425	21,7	381	1,085	80,95
0,212	43,71	424,71	2,19	78,76
0,15	42,09	466,81	2,10	76,66
0,075	87,43	554,23	4,37	72,29
0,075>	1445,77	2000	72,29	0

Hydrometer sieve analysis for sample T1C1

Sieve Size (mm)	Fraction passing %
0,212	97,3
0,15	94,7
0,075	89,3

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Sample T1C2:

Sieve analysis of sample T1C2

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	0	0	0	100
28	0	0	0	100
20	20,9	20,9	1,045	98,955
14	28,1	49	1,405	97,55
10	39,7	88,7	1,985	95,565
7,1	31,5	120,2	1,575	93,99
5	37,6	157,8	1,88	92,11
2	72,5	230,3	3,625	88,485
1	42,5	272,8	2,125	86,36
0,6	35	307,8	1,75	84,61
0,425	24,4	332,2	1,22	83,39
0,212	73,38	405,58	3,67	79,72
0,15	50,03	455,62	2,50	77,22
0,075	98,40	554,02	4,92	72,30
0,075>	1445,98	2000	72,30	0

Hydrometer sieve analysis for sample T1C2

Sieve Size (mm)	Fraction passing %
0,212	95,6
0,15	92,6
0,075	86,7

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Sample T1C3:

Sieve analysis of sample T1C3

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	77,9	77,9	3,895	96,105
28	107,2	185,1	5,36	90,745
20	37,8	222,9	1,89	88,855
14	72,9	295,8	3,645	85,21
10	59,9	355,7	2,995	82,215
7,1	55,9	411,6	2,795	79,42
5	56,2	467,8	2,81	76,61
2	111,8	579,6	5,59	71,02
1	51,2	630,8	2,56	68,46
0,6	34,7	665,5	1,735	66,725
0,425	21,3	686,8	1,065	65,66
0,212	70,91	757,71	3,55	62,11
0,15	42,02	799,74	2,10	60,01
0,075	84,04	883,78	4,20	55,81
0,075>	1116,22	2000	55,81	0

Hydrometer sieve analysis for sample T1C3

Sieve Size (mm)	Fraction passing %
0,212	94,6
0,15	91,4
0,075	85

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Sample T2C1:

Sieve analysis of sample T2C1

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	0	0	0	100
28	0	0	0	100
20	0	0	0	100
14	31,5	31,5	1,575	98,425
10	17,7	49,2	0,885	97,54
7,1	31,3	80,5	1,565	95,975
5	45,3	125,8	2,265	93,71
2	70,5	196,3	3,525	90,185
1	36,8	233,1	1,84	88,345
0,6	30,2	263,3	1,51	86,835
0,425	22	285,3	1,1	85,735
0,212	49,73	335,03	2,49	83,25
0,15	37,72	372,75	1,89	81,36
0,075	78,88	451,63	3,94	77,42
0,075>	1548,37	2000	77,42	0

Hydrometer sieve analysis for sample T2C1

Sieve Size (mm)	Fraction passing %
0,212	97,1
0,15	94,9
0,075	90,3

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Sample T2C2:

Sieve analysis of sample T2C2

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	0	0	0	100
28	52	52	2,6	97,4
20	25,6	77,6	1,28	96,12
14	36	113,6	1,8	94,32
10	25,4	139	1,27	93,05
7,1	35,5	174,5	1,775	91,275
5	45,5	220	2,275	89
2	80,8	300,8	4,04	84,96
1	45,1	345,9	2,255	82,705
0,6	36,3	382,2	1,815	80,89
0,425	26,6	408,8	1,33	79,56
0,212	42,96	451,76	2,15	77,41
0,15	41,37	493,13	2,07	75,34
0,075	85,92	579,06	4,30	71,05
0,075>	1420,94	2000	71,05	0

Hydrometer sieve analysis for sample T2C2

Sieve Size (mm)	Fraction passing %
0,212	97,3
0,15	94,7
0,075	89,3

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Sample T2C3:

Sieve analysis of sample T2C3

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	0	0	0	100
28	242,8	242,8	12,14	87,86
20	83,9	326,7	4,195	83,665
14	42,1	368,8	2,105	81,56
10	58,8	427,6	2,94	78,62
7,1	39,4	467	1,97	76,65
5	39,5	506,5	1,975	74,675
2	78,9	585,4	3,945	70,73
1	36,2	621,6	1,81	68,92
0,6	25,8	647,4	1,29	67,63
0,425	16,6	664	0,83	66,8
0,212	44,09	708,09	2,20	64,60
0,15	33,40	741,49	1,67	62,93
0,075	64,13	805,62	3,21	59,72
0,075>	1194,38	2000	59,72	0

Hydrometer sieve analysis for sample T2C3

Sieve Size (mm)	Fraction passing %
0,212	96,7
0,15	94,2
0,075	89,4

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Sample T1CS1:

Sieve analysis of sample T1CS1

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	246	246	12,3	87,7
28	146,2	392,2	7,31	80,39
20	100,8	493	5,04	75,35
14	107,6	600,6	5,38	69,97
10	85,8	686,4	4,29	65,68
7,1	57,9	744,3	2,895	62,785
5	62,8	807,1	3,14	59,645
2	110,2	917,3	5,51	54,135
1	57,7	975	2,885	51,25
0,6	45,9	1020,9	2,295	48,955
0,425	29,4	1050,3	1,47	47,485
0,212	188,04	1238,34	9,40	38,08
0,15	95,92	1334,26	4,80	33,29
0,075	154,80	1489,06	7,74	25,55
0,075>	510,94	2000	25,55	0

Hydrometer sieve analysis for sample T1CS1

Sieve Size (mm)	Fraction passing %
0,212	80,2
0,15	70,1
0,075	53,8

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Sample T1CS2:

Sieve analysis of sample T1CS2

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	196,3	196,3	9,815	90,185
28	120,6	316,9	6,03	84,155
20	116,8	433,7	5,84	78,315
14	78,9	512,6	3,945	74,37
10	50,7	563,3	2,535	71,835
7,1	64	627,3	3,2	68,635
5	65	692,3	3,25	65,385
2	125	817,3	6,25	59,135
1	68	885,3	3,4	55,735
0,6	56,1	941,4	2,805	52,93
0,425	36,6	978	1,83	51,1
0,212	170,67	1148,67	8,53	42,57
0,15	89,94	1238,61	4,50	38,07
0,075	164,54	1403,15	8,23	29,84
0,075>	596,85	2000	29,84	0

Hydrometer sieve analysis for sample T1CS2

Sieve Size (mm)	Fraction passing %
0,212	83,3
0,15	74,5
0,075	58,4

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Sample T1CS3:

Sieve analysis of sample T1CS3

Sieve size (mm)	mass retained (g)	Accum retained (g)	retained (%)	passing (%)
50	0	0	0	100
37,5	189,1	189,1	9,455	90,545
28	39,4	228,5	1,97	88,575
20	175,4	403,9	8,77	79,805
14	80,1	484	4,005	75,8
10	90	574	4,5	71,3
7,1	91,5	665,5	4,575	66,725
5	48,9	714,4	2,445	64,28
2	134,8	849,2	6,74	57,54
1	65,5	914,7	3,275	54,265
0,6	47,4	962,1	2,37	51,895
0,425	29,4	991,5	1,47	50,425
0,212	149,26	1140,76	7,46	42,96
0,15	73,62	1214,38	3,68	39,28
0,075	123,04	1337,42	6,15	33,13
0,075>	662,58	2000	33,13	0

Hydrometer sieve analysis for sample T1CS3

Sieve Size (mm)	Fraction passing %
0,212	85,2
0,15	77,9
0,075	65,7

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Hydrometer readings of all the samples.

Time	Original	T1C1	T2C1	T1C2	T2C2	T1C3	T2C3	T1CS1	T1CS2	T1CS3
40 sec	53	54	54	57	55	57	58	31	36	40
1 hour	29.5	34	32	37	31	37	28	14	16	23